Study of the synthesis of mixed dialkyl peroxides from metal alkyl peroxide and alkyl halide by phase transfer catalysis

Stefan Baj

Institute of Organic Chemistry and Technology, Silesian Technical University, ul. Krzywoustego 4, 44-100 Gliwice, Poland

Abstract

The kinetics of the reaction of the synthesis of selected mixed dialkyl peroxides from sodium and potassium organic peroxides in a two-phase solid/organic solvent system by phase transfer catalysis was studied. The effect of some parameters on the reaction rate was investigated. Pseudo-first-order kinetics can be used to describe the reaction rate. The apparent reaction rate constants were calculated and the activation energies of the reaction with different catalysts were determined.

Keywords: Peroxides; Synthesis; Phase transfer catalysis; Kinetics

1. Introduction

Aliphatic nucleophilic substitution employing organic hydroperoxides or their salts [1–8] as well as various alkyl derivatives is an important method for the synthesis of mixed organic peroxides:

$$R^1OOZ + R^2X \rightarrow R^1OOR^2 + ZX \qquad (1)$$

where: R^1, R^2 = alkyl; Z = H, Na or K; X = Br, Cl.

Aliphatic nucleophilic substitution is one of the most extensively investigated reactions in organic chemistry. The fundamental studies on the mechanism of these reactions have been presented by Ingold and co-workers [9]. Most of the known methods for the preparation of organic peroxides involve the above reaction performed in a homogenous system, usually in the presence of various additives. However these substances often cause undesirable side effects leading to a decomposition of the peroxides being formed thus reducing the selectivity of the reaction.

Reaction (1) can also be carried out in a two-phase system by phase transfer catalysis [10–15] as depicted in Scheme 1

Our previous work [11,14] was devoted to the synthesis of organic peroxides in a two-phase system in the presence of phase transfer catalysts. Pursuing the studies we extended their scope in order to generalize the method and to establish the optimum conditions of the reaction.

2. Results and discussion

A process of the preparation of organic peroxides according to the above scheme is per-

formed under conditions which favour nucle-ophilic substitution reaction S_N2. The rate law of this reaction generally obeys second order kinetics and the reaction rate depends on the concentration of both substrate and nucleophile. The kinetics of the process performed under the conditions of phase transfer catalysis appear to be more complex due to the problem of mass transfer encountered in addition to the chemical reactions [16,17]. Nevertheless when the process is performed with sufficiently vigorous stirring the system is within the kinetic region and the reaction proceeding in the organic phase is a rate-limiting process:

$$\frac{d[R^2X]}{d\tau} = -k[Q^+R^1OO^-][R^2X] \qquad (4)$$

As the rate of the $Q^+R^1OO^-$ ion pair forma-tion is considerably higher than that of the substitution reaction and the extent of side reac-tions in the initial stage of the process is small the $[Q^+R^1OO-]$ concentration can be considered as practically constant. Therefore the reaction rate can be described by the following equation:

$$\frac{d[R^2X]}{d\tau} = -k_{obs}[R^2X] \qquad (5)$$

where: $k_{obs} = k[Q^+R^1OO^-]$.

The conversion of alkyl halides is defined as:

$$x = 1 - \frac{[R^2X]}{[R^2X]_0} \qquad (6)$$

where: x conversion, $[R^2X]_0$ stands for the initial concentration and $[R^2X]$ is a concentra-tion of alkyl halide during the reaction.
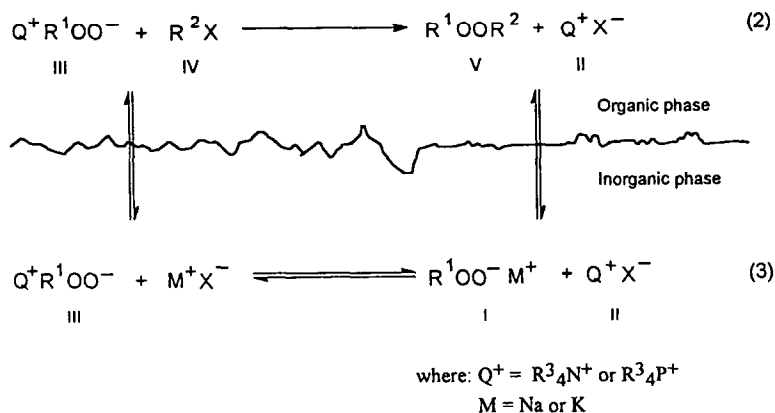
Combining Eqs. (5) and (6) we obtain:

$$\ln(1 - x) = -k_{obs}\tau \qquad (7)$$

The k_{obs} constants determined in the present study were utilized to analyse the process. The values of k_{obs} obtained for the reactions carried out at various temperatures were used to calcu-late the activation energy E_a. The calculations were performed according to Arrhenius equa-tion using the linear regression method.

2.1. Effect of agitation speed on the reaction rate

As mentioned above it is essential for the process to proceed within the kinetic region of the reaction. It was thus necessary to determine a limiting value of agitation speed above which practically no changes in the rate of the main product formation (i.e. organic peroxide) are observed. Such test was performed for the reac-tion of solid sodium cumyl peroxide I (R^1 = cumyl; M = Na) with n-butyl bromide IV (R^2 = n-Bu; X = Br) in the presence of tetra-n-butylammonium hydrogen sulfate as a catalyst II ($R^3 = n$-Bu) (Fig. 1). n-Butyl bromide was used as a solution in n-hexane. The plots of k_{obs} vs. the agitation speed are presented in Fig. 2. The reaction was observed to be highly affected

$$Q^+R^1OO^- + R^2X \longrightarrow R^1OOR^2 + Q^+X^- \qquad (2)$$
$$\quad\ \ \text{III} \qquad\quad \text{IV} \qquad\qquad\qquad\quad \text{V} \qquad\quad \text{II}$$

Organic phase

Inorganic phase

$$Q^+R^1OO^- + M^+X^- \rightleftharpoons R^1OO^-M^+ + Q^+X^- \qquad (3)$$
$$\quad\ \ \text{III} \qquad\quad\quad\qquad\qquad\qquad \text{I} \qquad\qquad \text{II}$$

where: $Q^+ = R^3_4N^+$ or $R^3_4P^+$

M = Na or K

Scheme 1.

by the interphase diffusion at low agitation speed. Above 800 rpm no significant improvement in the reaction rate was observed indicating the reaction to be within the kinetic region. Therefore the agitation speed was set at 1200 rpm for studying the reaction kinetics.

2.2. Influence of the structure of substrates on the course of the reaction

Alkyl bromides IV and metal organic peroxide I take part in the studied process as the reactants, with quaternary alkyl onium salts II or crown ethers as phase transfer catalysts. The influence of the structure of alkyl bromides IV (R^2 = Et, n-Pr, iso-Pr, n-Bu, iso-Bu, sec-Bu, Allyl, Bz; X = Br) on the course of the process was investigated for the reaction with sodium alkyl peroxides I (R^1 = cumyl; M = Na) in the presence of tetra-n-butylammonium hydrogen sulfate. The reaction was performed in a two-phase system, where I was a solid phase and a solution of IV in hexane served as a liquid phase. The plots of conversion vs. time of the

organic peroxide formation reactions are collected in Fig. 3.

The reactivity of the applied bromides were found to change in the following sequence:

Bz > Allyl > Et > n-Pr > n-Bu

> iso-Pr > iso-Bu > sec-Bu

Such dependences are typical for nucleophilic substitution reaction. The yields of the reactions of alkyl bromides are presented in Table 1 and the kinetic data are collected in Table 2. The results indicate that the proposed method allows the mixed organic peroxides to be obtain in high yields.

The other reactant used in the studied process is a metal organic peroxide consisting of a peroxide anion and a metal cation. The influence of the structure of a peroxide anion in a solid metal organic peroxide II (R^1 = cumyl, tert-Bu; M = Na) on the rate of a corresponding peroxide formation was studied for the reaction of II with n-butyl bromide IV (R^2 = Bu; X = Br) in the presence of tetra-n-butylammonium hydrogen sulfate. The reaction was performed in a two-phase system with II constituting one
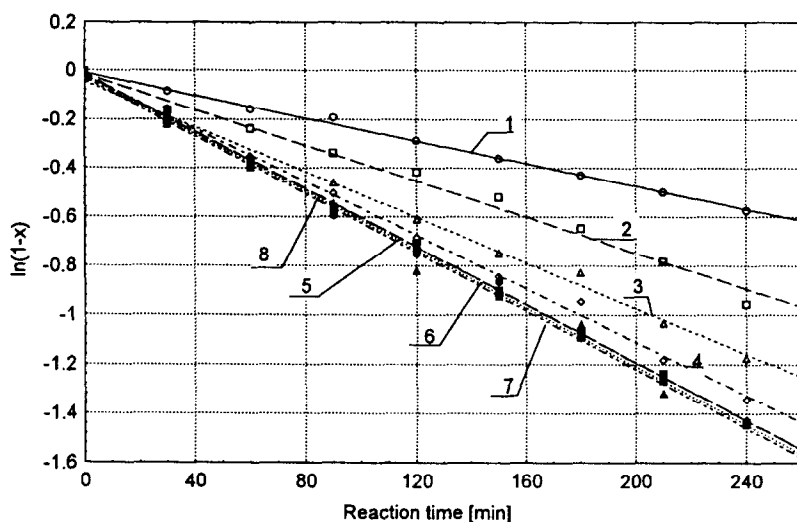

Fig. 1. Effect of agitation speed on conversion in the reaction of n-butyl bromide (1.150 mmol) with sodium cumyl peroxide (1.150 mmol) in the presence of tetra-n-butylammonium hydrogen sulfate (0.115 mmol) in n-hexane (3 cm³) at 60°C. Agitation speed: (1) 100 rpm; (2) 200 rpm; (3) 300 rpm; (4) 400 rpm; (5) 600 rpm; (6) 800 rpm; (7) 1000 rpm; (8) 1200 rpm.
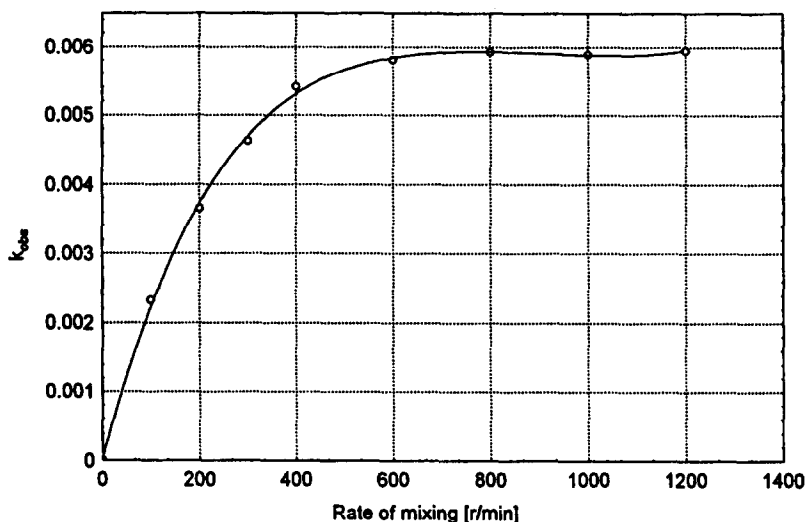
Fig. 2. Effect of agitation speed on conversion in the reaction of n-butyl bromide (1.150 mmol) with sodium cumyl peroxide (1.150 mmol) in the presence of tetra-n-butylammonium hydrogen sulfate (0.115 mmol) in n-hexane (3 cm^3) at 60°C.

phase and a solution of IV in hexane serving as the other phase (Fig. 4). From Fig. 4 it follows that the process of *tert*-butyl peroxide preparation proceeds with a higher rate compared to n-butyl cumyl peroxide preparation. This observation may be accounted for by a higher reactivity of *tert*-butyl peroxide anions as reported earlier [18,19].

The influence of the metal cation of a salt II (R^1 = cumyl; M = Na, K) was studied for the reaction of II with n-butyl bromide IV (R^2 = Bu; X = Br) in the presence of tetra-n-butylammonium hydrogen sulfate. The reaction was carried out in a two-phase system where solid II and a solution of IV in hexane were the respective phases (Fig. 5). The rate of formation of the
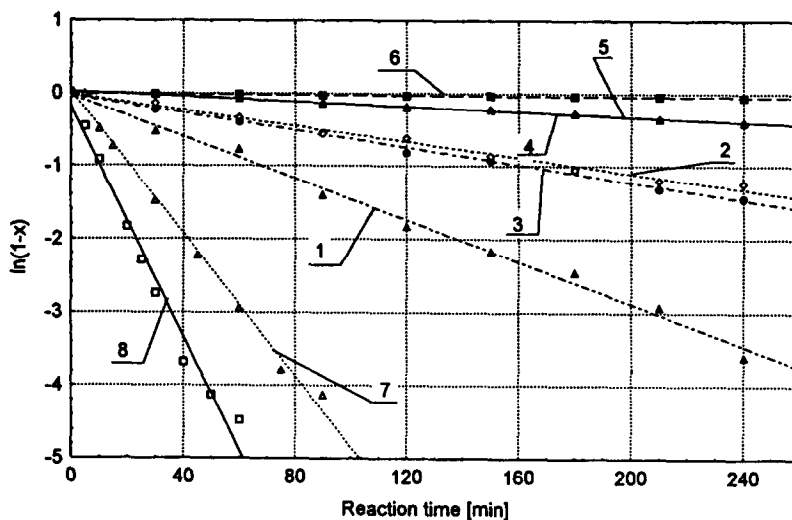

Fig. 3. Comparison of the reactivity of different alkyl bromides (1.150 mmol) with sodium cumyl peroxide (1.150 mmol) in the presence of tetra-n-butylammonium hydrogen sulfate (0.115 mmol) in n-hexane (3 cm^3) at 60°C. 1-Ethyl bromide; (2) n-propyl bromide; (3) n-butyl bromide; (4) *iso*-propyl bromide; (5) *iso*-butyl bromide 6) *sec*-butyl bromide; (7) allyl bromide; (8) benzyl bromide.

corresponding peroxide from potassium salt was found to be higher than that observed for sodium salt. Plot 3 in Fig. 5 depicts the process of the formation of n-butyl cumyl peroxide in a two-phase system with sodium hydroxide serving as a solid phase and a solution of cumyl hydroperoxide and n-butyl bromide in hexane constituting a liquid phase. The rate of the process performed in this way was found to be considerably lower than that observed for a system with sodium cumyl peroxide. The process employing metal organic peroxide thus appears to be more efficient from the kinetic point of view.

2.3. Influence of the structure of catalysts on the course of the reaction

Within the scope of our studies two groups of phase transfer catalysts were tested: (i) quaternary onium salts; (ii) crown ethers.

The rates of n-butyl cumyl peroxide V (R^1 = cumyl; R^2 = n-Bu) formation in the reaction of solid sodium cumyl peroxide I (R^1 = cumyl; M = Na) with n-butyl bromide IV (R^2 = n-Bu) carried out in benzene solution with various catalysts were compared. The following catalysts were employed: tetraalkylammonium salts

(tetra-n-butylammonium chloride and benzyltriethylammonium chloride), tetraalkylphosphonium salts (tetra-n-butylphosphonium chloride) and crown ethers (15-crown-5 and 18-crown-6). The results presented in Fig. 6 clearly demonstrate the process of peroxide preparation to proceed faster in the presence of onium salts as compared to the crown ethers. From the group of onium salts tetra-n-butylammonium salts are recommended for use. 15-crown-5 appears to be the most effective crown ether which may be attributed to its highest ability to transfer sodium cation to the organic phase. The catalytic activity of the ethers under study was found to decrease as follows:

15-crown-5 > 18-crown-6
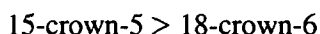
being consistent with the literature data concerning the activity of such systems in other reactions [20,21].

The catalytic activity of quaternary onium salts was found to be closely related to the type of the respective anion. The results of our experiments carried out in order to determine this dependence are shown in Fig. 7.

The study was performed for the reaction of a solid sodium cumyl peroxide with n-butyl

Table 1
Synthesis of mixed dialkyl peroxides from alkyl bromides (0.05 mol) and sodium alkyl peroxides (0.05 mol) with tetra-n-butylammonium hydrogen sulfate as catalyst (0.005 mol) in n-hexane (130 ml) at 60°C under Ar

Entry	Reaction	Product	HPLC method [a]		Isolated products [b]	
			Reaction time min	Yield %	Reaction time min	Yield %
1	EtBr + $C_6H_5C(CH_3)_2$OONa	$C_6H_5C(CH_3)_2$OOEt	120	91.13	180	78.3
2	n-PrBr + $C_6H_5C(CH_3)_2$OONa	$C_6H_5C(CH_3)_2$OO(n-Pr)	120	90.16	240	81.4
3	iso-PrBr + $C_6H_5C(CH_3)_2$OONa	$C_6H_5C(CH_3)_2$OO(iso-Pr)	120	86.32	240	68.6
4	n-BuBr + $C_6H_5C(CH_3)_2$OONa	$C_6H_5C(CH_3)_2$OO(n-Bu)	120	88.54	300	81.4
5	iso-BuBr + $C_6H_5C(CH_3)_2$OONa	$C_6H_5C(CH_3)_2$OO(iso-Bu)	120	85.35	360	78.3
6	sec-BuBr + $C_6H_5C(CH_3)_2$OONa	$C_6H_5C(CH_3)_2$OO(sec-Bu)	120	80.73	360	68.2
7	AllylBr + $C_6H_5C(CH_3)_2$OONa	$C_6H_5C(CH_3)_2$OOAllyl	120	76.15	360	54.7
8	BzBr + $C_6H_5C(CH_3)_2$OONa	$C_6H_5C(CH_3)_2$OOBz	120	83.24	300	65.2
9	n-BuBr + t-BuOONa	t-BuOO(n-Bu)	120	91.05	360	80.4
10	iso-BuBr + t-BuOONa	t-BuOO(iso-Bu)	120	88.31	360	76.1
11	sec-BuBr + t-BuOONa	t-BuOO(sec-Bu)	120	82.34	360	72.8

[a] Determined by quantitative HPLC analysis (LiChrosorb RP18 10 μm; MeOH:H_2O 75:25, 1 ml/min).
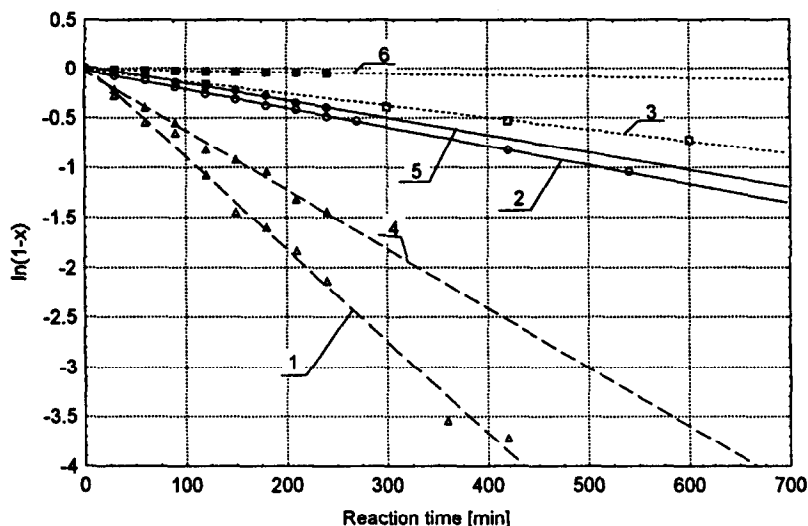[b] Yields based on isolated products by gravity column chromatography.

Fig. 4. Comparison of the reactivity of butyl bromides (1.150 mmol) with sodium *tert*-butyl peroxide and sodium cumyl peroxide (1.150 mmol) in the presence of tetra-*n*-butylammonium hydrogen sulfate (0.115 mmol) in *n*-hexane (3 cm³) at 60°C. (1) *n*-Butyl bromide, (2) *iso*-butyl bromide and (3) *sec*-butyl bromide with sodium *tert*-butyl peroxide and (4) *n*-butyl bromide, (5) *iso*-butyl bromide, (6) *sec*-butyl bromide with sodium cumyl peroxide in the presence of tetra-*n*-butyl hydrogen sulfate.

bromide carried out in a benzene solution in the presence of tetra-*n*-butylammonium hydrogen sulfate, chloride and bromide. The catalytic activity was found to change in the following manner:

$$HSO_4^- > Br^- > Cl^-$$
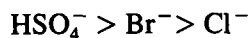
and to be inversely proportional to the anion ability to associate with the ammonium cation.

The influence of the amount of catalyst was studied for the reaction of solid sodium cumyl peroxide with *n*-butyl bromide carried out in a benzene solution in the presence of tetra-*n*-butylammonium hydrogen sulfate. Fig. 8 dis-
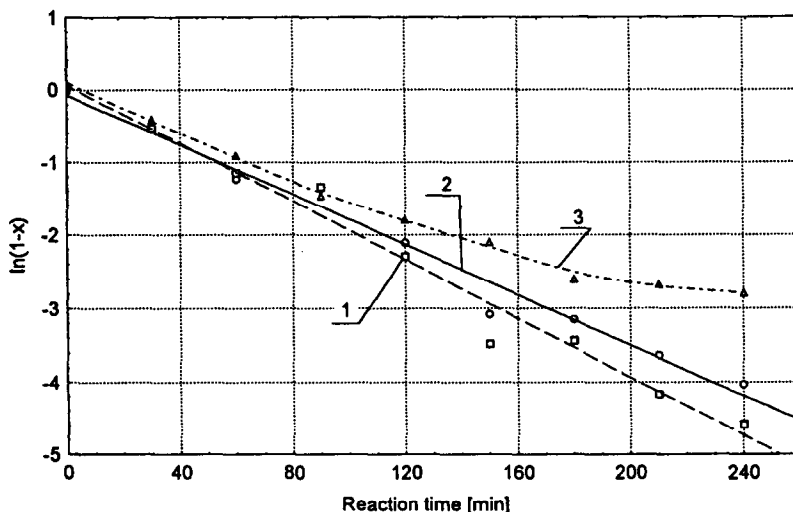

Fig. 5. Comparison of the reactivity of potassium cumyl peroxide (1) and sodium cumyl peroxide (1.150 mmol), (2) with *n*-butyl bromide (1.150 mmol) in the presence of tetra-*n*-butylammonium hydrogen sulfate (0.115 mmol) in *n*-hexane (3 cm³) at 60°C. (3) Plot for the reaction of cumyl peroxide (1.150 mmol) with *n*-butyl bromide (1.150 mmol) in the presence of NaOH (1.150 mmol) and tetra-*n*-butylammonium hydrogen sulfate (0.115 mmol).
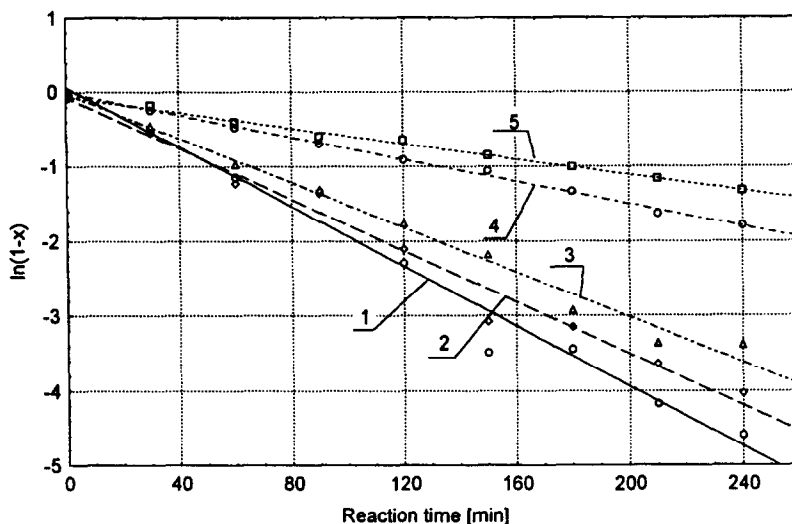
Fig. 6. Effects of the catalysts (0.115 mmol) on conversion in the reaction of n-butyl bromide (1.150 mmol) with sodium cumyl peroxide (1.150 mmol) in n-hexane (3 cm^3) at 60°C in the presence of: (1) tetra-n-butylammonium chloride; (2) triethylbenzylammonium chloride; (3) tetra-n-butylphosphonium chloride; (4) 15-crown-5; 18-crown-6.

plays the plots of $\ln(1 - x)$ vs. time of the reaction. The results demonstrate the rate of the process to depend on the amount of catalyst, the dependence being directly proportional (Fig. 9).

2.4. Effects of the solvent on the reaction course

In the phase transfer-catalyzed reaction the choice of a solvent dramatically affects the conversion. n-Hexane, benzene, toluene and chlorobenzene were utilized in our study to illustrate this problem. A study was performed for the reaction of a solid sodium cumyl peroxide with solution n-butyl bromide in a given solvent. The results are shown in Fig. 10. As seen a higher conversion and higher reaction
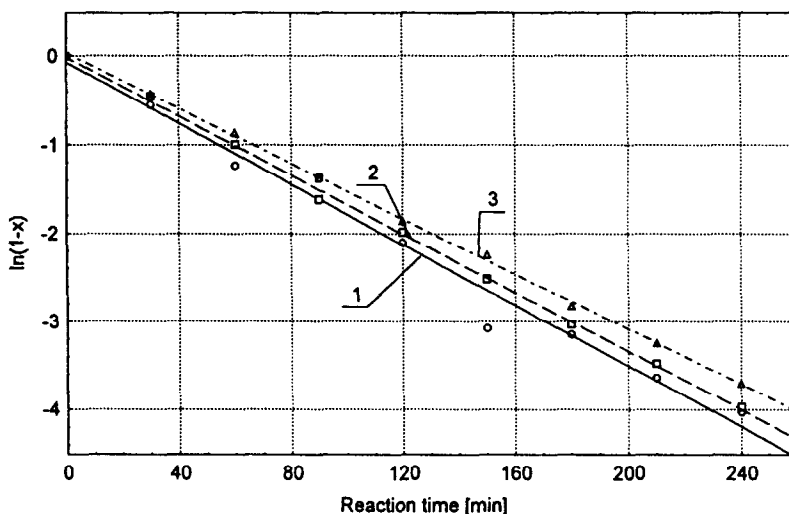

Fig. 7. Effect of the anion in tetraalkylammonium salt on conversion in the reaction of n-butyl bromide (1.150 mmol) with sodium cumyl peroxide (1.150 mmol) in the presence of tetra-n-butylammonium salt (0.115 mmol) in n-hexane (3 cm^3) at 60°C: (1) tetra-n-butylammonium hydrogen sulfate; (2) tetra-n-butylammonium bromide; (3) tetra-n-butylammonium chloride.
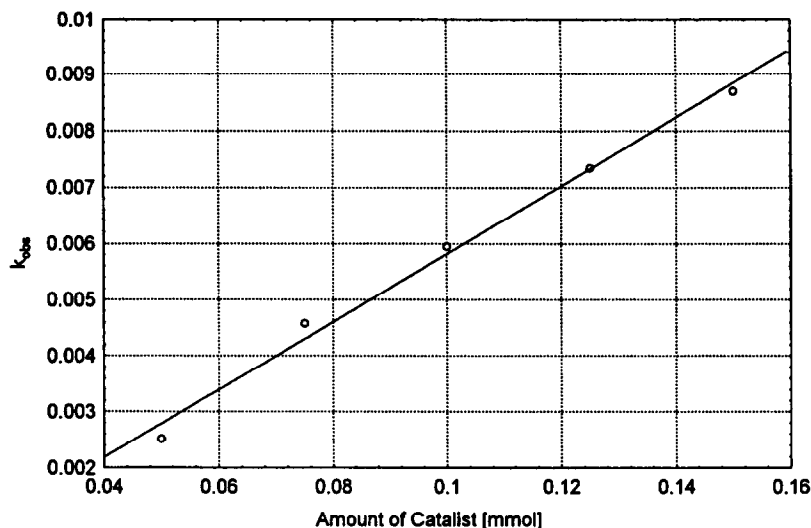
Fig. 8. Dependence on the conversion in the reaction of *n*-butyl bromide (1.150 mmol) with sodium cumyl peroxide (1.150 mmol) in *n*-hexane (3 cm^3) at 60°C in presence of tetra-*n*-butylammonium hydrogen sulfate on the amounts of the catalyst: (1) 0.15 mmol ; (2) 0.125 mmol; (3) 0.10; (4) 0.075 mmol; (5) 0.05 mmol.

rate were obtained in chlorobenzene due to the high polarity of this solvent. The order of the relative activities of the studied solvents is:

chlorobenzene > toluene > benzene ≫ *n*-hexane

The data obtained indicate that better reactivity is achieved in a protic or polar solvent.

2.5. Effects of the water on the reaction course

Sodium and potassium organic peroxides are known to be highly hygroscopic substances. They are obtained as hydrates containing ca. 40% of water [22] using conventional methods involving the reaction of organic hydroperox-
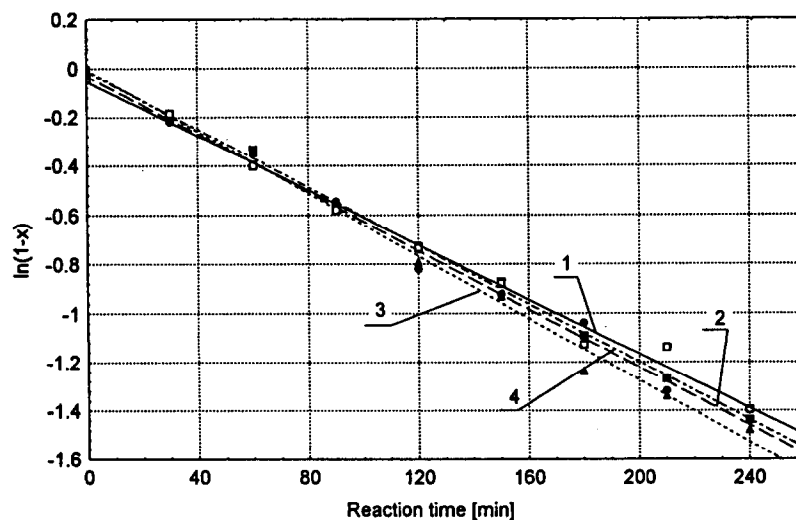

Fig. 9. Effects of the amounts of the catalyst on conversion in the reaction of *n*-butylbromide (1.150 mmol) with sodium cumyl peroxide (1.150 mmol) in the presence of tetra-*n*-butylammonium hydrogen sulfate in *n*-hexane (3 cm^3) at 60°C.
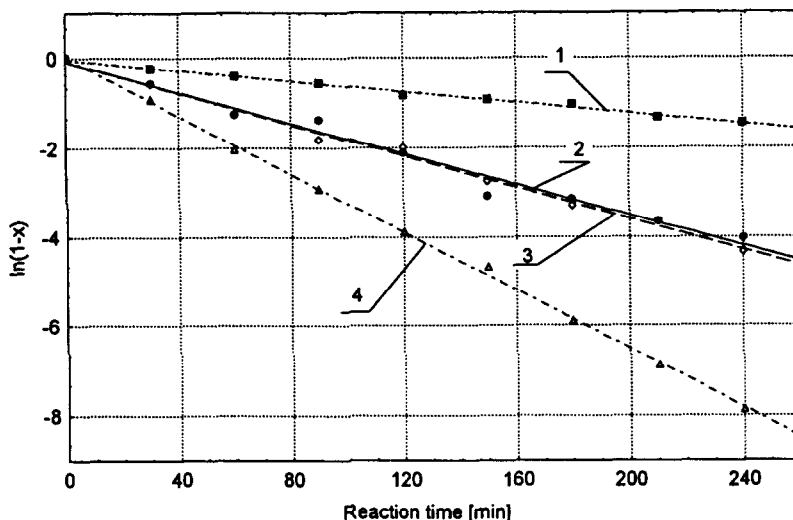
Fig. 10. Effects of solvents on conversion in the reaction of n-butylbromide (1.150 mmol) with sodium cumyl peroxide (1.150 mmol) in the presence of tetra-n-butylammonium hydrogen sulfate (0.115 mmol) at 60°C in (3 cm^3): (1) hexane; (2) benzene; (3) toluene; (4) chlorobenzene.

ides with their respective hydroxides. Anhydrous forms of these substances can be produced only in the reaction of organic hydroperoxides with sodium or potassium amide [23]. It was thus interesting to reveal the influence of water on the course of the studied process. A study was performed for the reactions of solid sodium cumyl peroxide with n-butyl bromide carried out in solution in n-hexane. The results

of the measurements are presented in Fig. 11. The rate of the reactions under study was found to be practically independent of water content in solid sodium cumyl peroxide.

2.6. Effects of temperature

The following operating conditions were used: 1.150 mmol of corresponding alkyl bro-
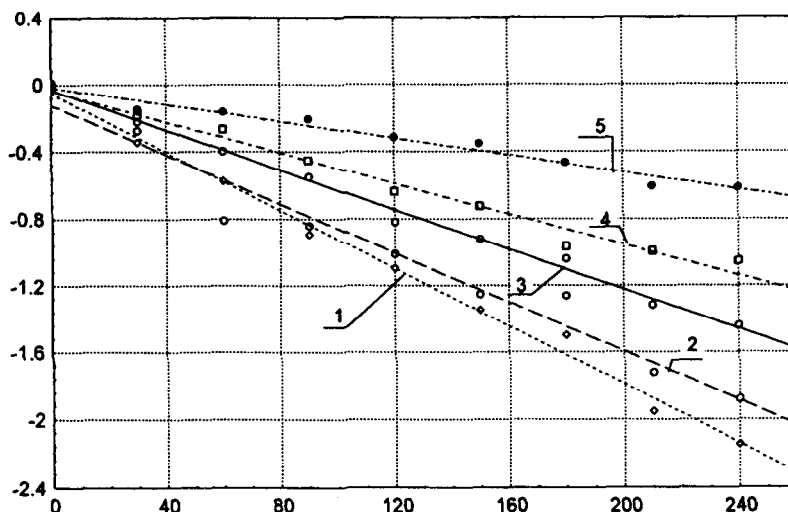
Fig. 11. Effects of the volume ratio (%) of water to sodium cumyl peroxide on the conversion for reaction of n-butyl bromide (1.150 mmol) with sodium cumyl peroxide (1.150 mmol) in presence of tetra-n-butylammonium hydrogen sulfate (0.115 mmol) in n-hexane (3 cm^3) at 60°C. S = (1) 0; (2) 10; (3) 30 4) 40.

Table 2
Kinetic data of the reactions of the synthesis of mixed dialkyl peroxides from alkyl bromides (0.05 mol) and sodium alkyl peroxides (0.05 mol) with tetra-n-butylammonium hydrogen sulfate (0.005 mol) as catalyst in n-hexane under Ar

Entry	$\log(1-x) = a + k_{obs} \cdot \tau$ [a]			$k_{obs} = A \cdot e^{-E_a/RT}$ [b]		
	a	$k_{obs} \cdot 10^5$ [s^{-1}]	R	A	E_a [kJ/mol]	R
1	−0.025	23.33	0.996	$9.8 \cdot 10^6$	57	0.747
2	−0.016	9.0	0.994	$1.9 \cdot 10^7$	61	0.911
3	0.028	3.0	0.992	$1.2 \cdot 10^7$	64	0.787
4	−0.030	10.00	0.997	$9.9 \cdot 10^7$	65	0.954
5	0.0058	3.83	0.982	$2.7 \cdot 10^8$	84	0.905
6	−0.017	0.33	0.996	$3.5 \cdot 10^8$	91	0.907
7	−0.074	161.67	0.993	–	–	–
8	−0.37	266.67	0.993	–	–	–
9	0.030	15.50	0.995	$6.6 \cdot 10^7$	63	0.941
10	−0.019	3.17	0.999	$1.9 \cdot 10^8$	70	0.914
11	−0.013	2.0	00.994	$6.3 \cdot 10^8$	81	0.901

[a] At 60°C.

[b] From four determinations at 60, 55, 50, 45 and 40°C.

mides (R^2 = Et, n-Pr, iso-Pr, n-Bu, iso-Bu, sec-Bu, X = Br), 1.150 mmol sodium alkyl peroxides (R^1 = cumyl, tert-Bu, M = Na), 0.115 mmol tetra-n-butylammonium hydrogen sulfate and 3 cm³ n-hexane to study the effect of temperature on the reaction course of alkyl bromide with sodium alkyl peroxides. The investi-

gations were carried out at 60, 55, 50, 45, 40°C. An Arrhenius plots of $\ln(k_{obs})$ vs. $1/T$ of the corresponding reaction are given in Fig. 12. The activation energies E_a are collected in Table 2. The E_a values are among 57 to 91 kcal/mol. This facts may be a confirmation of our previous observation that the reactions proceed in a kinetic region.

3. Conclusion

The alkylation of metal organic peroxides with alkyl bromides in a two-phase system by phase transfer catalysis were carried out. Several organic peroxides were obtained in high yields. The influence of the structure of alkyl substituent on the course of the reaction typical for nucleophilic substitution was observed: Bz > Allyl > Et > n-Pr > n-Bu > iso-Pr > iso-Bu > sec-Bu. Sodium tert-butyl peroxide was found to react more readily with alkyl bromides than with sodium cumyl peroxides which is consistent with previous observations. Several phase transfer catalysts were tested and tetra-n-butylammonium hydrogen sulfate was
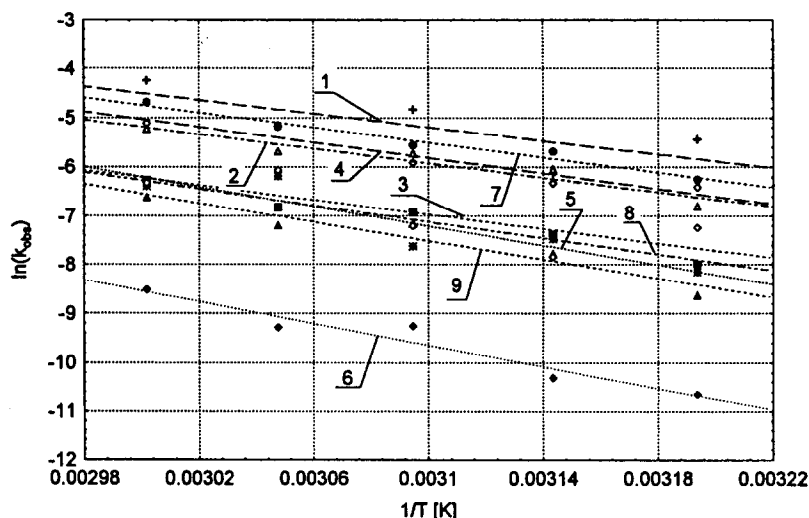
Fig. 12. Arrhenius plot for reaction of synthesis of different dialkyl peroxides from alkyl bromides (1.150 mmol) with sodium alkyl peroxide (1.150 mmol) in presence of tetra-n-butylammonium hydrogen sulfate (0.115 mmol) in n-hexane (3 cm³): (1) Ethyl cumyl peroxide; (2) n-propyl cumyl peroxide; (3) iso-propyl cumyl peroxide; (4) n-butyl cumyl peroxide; (5) iso-butyl cumyl peroxide; (6) sec-butyl cumyl peroxide; (7) n-butyl tert-butyl peroxide; (8) iso-butyl tert-butyl peroxide; (9) sec-butyl tert-butyl peroxide.

demonstrated to be the most efficient catalyst. The order of the relative activities for solvents is: chlorobenzene > toluene > benzene ≫ n-hexane. Pseudo-first-order kinetics can be used to represent the reaction mechanism when the reaction is carried out with an excess amount of metal alkyl peroxide relative to alkyl bromide. The developed method is very convenient for the preparation of mixed organic peroxides.

4. Experimental

4.1. Materials

n-Butyl bromide, iso-butyl bromide, sec-butyl bromide, ethyl bromide, n-propyl bromide and iso-propyl bromide were commercial materials (Merck, Darmstadt); cumyl peroxide [24] and tert-butyl peroxide [25] were prepared from their respective hydroperoxides according to the known procedures. n-Hexane and methanol used as eluent for HPLC were HPLC grade.

4.2. Procedures

^{1}H and ^{13}C NMR spectra of tetra-alkylammonium alkyl peroxide in deuterobenzene and dialkylperoxides in deuterochloroform were recorded on a Varian VXR-300 spectrometer operating at the ^{1}H resonance frequency of 300 MHz and the ^{13}C resonance frequency of 75 MHz. Chemical shifts (in ppm) were referenced relative to tetramethylsilane (TMS) as an internal standard. Infrared spectra were measured as neat films. Analytical high-performance liquid chromatography was performed on a Philips LX liquid chromatograph with a Philips XPD spectrophotometric detector ($\lambda = 256$ nm) and Merck Glass Cartridge Column with LiChrosorb RP 18 or Merck Glass Cartridge Column LiChrosorb Si 60 (150 × 2 mm, 5 μm). Solvent systems include Method A (methanol/water, 75/25, 1.0 ml/min) [26] or method B (hexane/iso-propanol, 99.25/0.75, 1.0 ml/min) [27]. Elemental analyses were per-

formed on Perkin Elmer equipment. Active oxygen in peroxide substances was determined by iodometric method [28].

4.2.1. Reaction of alkyl peroxides with metal organic peroxide. General procedure

To a solution oh the alkyl bromides (1.150 mmol) and PTC catalyst (0.115 mmol) in dry organic solvent (3 cm^3) under argon, metal organic peroxide (1.150 mmol) was added in one portion. The mixture was stirred (beyond 1200 rpm). The course of reaction was controlled by HPLC and GC method. At the and reaction products were analysed for content of unreacted metal organic peroxides by iodometric titration.

4.2.2. Preparation of dialkyl peroxides. General procedure

Alkyl bromide (0.05 mol), sodium organic peroxide (0.05 mol) and tetra-n-butylammonium-hydrogen sulfate (0.005 mol) were stirred in 130 cm^3 of benzene at 50°C. Reaction times are given in Table 1. Then the reaction mixture was washed with water, dried (MgSO$_4$) and evaporated in vacuum). Residue as colorless oil was separated by column chromatography using silica gel 50/100 mesh and eluent consisting of hexane and isopropyl alcohol (99:1).

4.2.2.1. Ethyl cumyl peroxide.
^{1}H NMR (CDCl$_3$) δ 0.98 (t, $J = 7.0$, 3H, –CH$_3$), 1.61 (s, 6H, C(CH$_3$)$_2$), 2.79 (q, $J = 7.0$, 2H, O–CH$_2$–) (m 5H, C$_6$H$_5$); ^{13}C NMR (CDCl$_3$) δ 145.62, 128.45, 128.11, 127.86 (C$_6$H$_5$), 82.61 ((CH$_3$)$_2$C–OO), 70.12.21 (C–O), 13.13 (CH$_3$). Anal. Calcd. for C$_{11}$H$_{16}$O$_2$: C, 73.30; H, 8.95. Found: C, 73.11; H, 9.00. Calcd. active peroxy oxygen 17.75%. Found 17.65%.

4.2.2.2. n-Propyl cumyl peroxide.
^{1}H NMR (CDCl$_3$) δ 0.84 (t, $J = 7.0$, 3H, –CH$_3$), 1.33 (br m, 2H, –CH$_2$–), 1.77 (s, 6H, –C(CH$_3$)$_2$), 2.96 (br t, 2H, O–CH$_2$–), 7.36 (m, 5H, C$_6$H$_5$); ^{13}C NMR (CDCl$_3$) δ 145.72, 128.34, 127.82,

126.77 (C_6H_5), 82.61 ((CH_3)$_2$C–OO), 77.07 (–C–OO), 26.62 ((CH_3)$_2$), 21.23 (CH_2), 10.52 (CH_3). Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 75.99; H, 9.25. Calcd. active peroxy oxygen 16.47%. Found 16.63%.

4.2.2.3. iso-Propyl cumyl peroxide. ^{1}H NMR (CDCl$_3$) δ 0.84 (d, $J = 7.0$, 6H, –CH$_3$), 1.77 (s, 6H, –C(CH$_3$)$_2$), 2.96 (br t, 1H, O–CH–), 7.36 (m, C$_6$H$_5$); ^{13}C NMR (CDCl$_3$) δ 144.82, 128.34, 127.82, 126.77, 83.73 ((CH$_3$)$_2$C–OO), 77.83 (C–OO), 26.91 ((CH$_3$)$_2$), 21.65 (CH$_2$), 10.67 (CH$_3$). Anal. Calcd. for C$_{12}$H$_{18}$O$_2$: C, 74.19; H, 9.34. Found: C, 74.25; H, 9.21. Calcd. active peroxy oxygen 16.47%. Found 17.01%.

4.2.2.4. n-Butyl cumyl peroxide. ^{1}H NMR (CDCl$_3$) δ 0.76 (t, $J = 6.4$, 3H, –CH$_3$), 1.07 (m, 2H, –CH$_2$–), 1.39 (m, 2H, –CH$_2$–), 1.57 (s, 6H, –C(CH$_3$)$_2$), 3.80 (t, 2H, O–CH$_2$–), 7.13 (m, 5H, C$_6$H$_5$–); ^{13}C NMR (CDCl$_3$) δ 147.28, 128.24, 127.67, 127.75, 127.67, 128.15, 82.75 (C–OO), 60.03 (C–O), 27.05 ((CH$_3$)$_2$, –CH$_2$–), 15.66 (–CH$_2$), 11.07 (CH$_3$). Anal. Calcd. for C$_{13}$H$_{20}$O$_2$: C, 74.96; H, 9.68. Found: C, 74.12; H, 9.43. Calcd. active peroxy oxygen 15.36%. Found 15.01%.

4.2.2.5. iso-Butyl cumyl peroxide. ^{1}H NMR (CDCl$_3$) δ 0.78 (d, $J = 6.6$, 6H, (–CH$_3$)$_2$), 1.57 (s, 6H, –C(CH$_3$)$_2$), 3.61 (d, $J = 6.6$, O–CH$_2$–), 7.37 (m, C$_6$H$_5$); ^{13}C NMR (CDCl$_3$) δ 147.28, 128.24, 127.67, 127.75, 127.67, 128.15, 82.75 (C–OO), 60.03 (C–O), 27.05 ((CH$_3$)$_2$, –CH$_2$–), 15.66 (–CH$_2$), 11.07 (CH$_3$). Anal. Calcd. for C$_{13}$H$_{20}$O$_2$: C, 74.96; H, 9.68. Found: C, 74.07; H, 9.56. Calcd. active peroxy oxygen 15.36%. Found 15.75%.

4.2.2.6. sec-Butyl cumyl peroxide. ^{1}H NMR (CDCl$_3$) δ 0.71 (t, $J = 6.6$, 3H, –CH$_3$), 1.09 (d, $J = 6.6$, 3H, –CH$_3$), 1.17 (quin, 2H, –CH$_2$–), 1.58 (s, –(CH$_3$)2) 3.79 (sextet, $J = 6.6$, 1H, O–CH–), 7.15 (m, 5H, C$_6$H$_5$–); ^{13}C NMR (CDCl$_3$) δ 147.28, 128.24, 127.67, 127.67, (C$_6$H$_5$), 82.75 (C–OO), 60.03 (C–O),

27.05 ((CH$_3$)$_2$, –CH$_2$–), 15.66 (–CH$_2$), 11.07 (CH$_3$). Anal. Calcd. for C$_{13}$H$_{20}$O$_2$: C, 74.96; H, 9.68. Found: C, 74.18; H, 9.39. Calcd. active peroxy oxygen 15.36%. Found 14.93%.

4.2.2.7. Allyl cumyl peroxide. ^{1}H NMR (CDCl$_3$) δ 4.87 (m, $J = 6.6$, 1H, –CH=), 4.29 (d, $J = 6.4$, 2H, =CH$_2$–), 3.54 (d, $J = 6.4$, 2H, –O–CH$_2$–), 1.58 (s, –(CH$_3$)2) 6.95 (m, 5H, C$_6$H$_5$–); ^{13}C NMR (CDCl$_3$) δ 145.44, 128.63, 128.21, 128.02, (C$_6$H$_5$), 82.93 (C–OO), 76.03 (C–O), 26.62 ((CH$_3$)$_2$, –CH$_2$–), 124.39 (–CH$_2$) 118.57 (CH). Anal. Calcd. for C$_{12}$H$_{16}$O$_2$: C, 74.97; H, 8.39. Found: C, 74.88; H, 8.21. Calcd. active peroxy oxygen 16.64%. Found 15.19%.

4.2.2.8. Benzyl cumyl peroxide. ^{1}H NMR (CDCl$_3$) δ 1.52 (s, –(CH$_3$)$_2$), 5.11 (s, 2H, O–CH$_2$–), 7.15 (m, 10H, 2C$_6$H$_5$–); ^{13}C NMR (CDCl$_3$) δ 147.28, 128.24, 127.67, 127.67, 2 (C$_6$H$_5$), 82.96 (C–OO), 60.03 (C–O), 27.05 ((CH$_3$)$_2$, –CH$_2$–), 15.66 (–CH$_2$), Anal. Calcd. for C$_{16}$H$_{18}$O$_2$: C, 79.31; H, 7.49. Found: C, 79.21; H, 7.39. Calcd. active peroxy oxygen 13.21%. Found 12.11%.

4.2.2.9. n-Butyl tert-butyl peroxide. ^{1}H NMR (CDCl$_3$) δ 0.76 (t, $J = 6.4$, 3H, –CH$_3$), 1.07 (m, $J = 6.4$, 2H, –CH$_2$–), 1.39 (m, $J = 6.4$, 2H, –CH$_2$–), 1.57 (s, 9H, –C(CH$_3$)$_3$), 3.81 (t, 2H, O–CH$_2$–), ^{13}C NMR (CDCl$_3$) δ 147.28, 128.24, 127.67, 127.75, 127.67, 128.15, 82.75 (C–OO), 60.03 (C–O), 27.05 ((CH$_3$)$_2$, –CH$_2$–), 15.66 (–CH$_2$), 11.07 (CH$_3$). Anal. Calcd. for C$_8$H$_{18}$O$_2$: C, 65.71; H, 12.41. Found: C, 65.59; H, 12.39. Calcd. active peroxy oxygen 21.88%. Found 22.35%.

4.2.2.10. iso-Butyl tert-butyl peroxide. ^{1}H NMR (CDCl$_3$) δ 0.78 (d, $J = 6.6$, 6H, (–CH$_3$)$_2$), 1.57 (s, 6H, –C(CH$_3$)$_2$), 3.61 (d, $J = 6.6$, O–CH$_2$–), 7.37 (m, C$_6$H$_5$–); ^{13}C NMR (CDCl$_3$) δ 147.28, 128.24, 127.67, 127.75, 127.67, 128.15, 82.75 (C–OO), 60.03 (C–O), 27.05 ((CH$_3$)$_2$, –CH$_2$–), 15.66 (–CH$_2$), 11.07 (CH$_3$). Anal. Calcd. for C$_{13}$H$_{20}$O$_2$: C, 74.96; H, 9.68. Found:

C, 74.07; H, 9.56. Calcd. active peroxy oxygen 15.36%. Found 15.75%.

4.2.2.11. sec-Butyl tert-butyl peroxide. ^{1}H NMR (CDCl$_3$) δ 0.71 (t, *J* = 6.6, 3H, –CH$_3$), 1.09 (d, *J* = 6.6, 3H, –CH$_3$), 1.17 (quin, 2H, –CH$_2$–), 1.58 (s, –(CH$_3$)2) 3.79 (sextet, *J* = 6.6, 1H, O–CH–), 7.15 (m, 5H, C$_6$H$_5$–); ^{13}C NMR (CDCl$_3$) δ 147.28, 128.24, 127.67, 127.67, (C$_6$H$_5$), 82.75 (C–OO), 60.03 (C–O), 27.05 ((CH$_3$)$_2$, –CH$_2$–), 15.66 (–CH$_2$), 11.07 (CH$_3$). Anal. Calcd. for C$_{13}$H$_{20}$O$_2$: C, 74.96; H, 9.68. Found: C, 74.18; H, 9.39. Calcd. active peroxy oxygen 15.36%. Found 14.93%.

References

[1] M.F. Salomon, R.G. Salomon and R.D. Gleim, J. Org. Chem., 41 (1976) 3983.

[2] F.H. Dickey and F.R. Bell, US Pat. 2 403 709 (1946).

[3] N.A. Milas and D.M. Surgenor, J. Am. Chem. Soc., 68 (1946) 206.

[4] F.F. Rust, F.H. Seubold and W.E. Waugh, J. Am. Chem. Soc., 72 (1950) 338.

[5] T.W. Cambell and G.M. Coppinger, J. Am. Chem. Soc., 73 (1951) 1789.

[6] P.G.Cookson, B.P. Roberts and A.G. Davies, Br. Pat. 1 588 870 (1981) (CA 95: 203314q).

[7] T.W. Cambell and G.M. Coppinger, J. Am. Chem. Soc., 73 (1951) 1788.

[8] F. Welch, H.R. Williams and H.S. Mosher, J. Am. Chem. Soc., 77 (1955) 551.

[9] C.K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell Univ. Press, Ithaca, NY, 1969.

[10] N. Hideo and S.Vashiko, Jpn. Pat. 51-110 504 (1975) (CA 86; 72197t).

[11] S. Baj and Z. Kulicki, Presented at Annual Conference of Polish Chemical Society, Gliwice, 6–9 September 1989.

[12] M.-J. Bourgeois, E. Montaudon and B. Maillard, Synthesis, 9 (1989) 700.

[13] J. Moulines, M.-J. Bourgeois, M. Campangole, A.-M. Limidey, B. Maillard and E. Montaudon, Synth. Commun., 20 (1990) 349.

[14] S. Baj, Pol. J. App. Chem., 30 (1991) 137.

[15] M.-J. Bourgeois, E. Montaudon and B. Maillard, Tetrahedron, 49 (1993) 2477.

[16] E. V. Dehmlow and S.S. Dehmlow, Phase Transfer Catalysis, Verlag Chimie, Weinheim, 1983.

[17] M. Makosza and M. Ferodyński, Adv. Catal., 35 (1987) 375.

[18] S. Baj, Polym. J. Chem., 68 (1994) 1559.

[19] S. Baj and M. Dawid, J. Mol. Struct. (Theochem), 306 (1994) 67.

[20] C.M. Starks and C. Liotta, Phase Transfer Catalysis Principles and Techniques, Academic Press, New York, 1978.

[21] F. Montanari, D. Landini and F. Rolla, Top. Curr. Chem., 101 (1982) 148.

[22] N.A. Sokolov and J. A. Aleksandrov, Usp. Khim., 47 (1978) 307.

[23] A. Riecche and J. Dahlmann, Liebigs Ann. Chem., 675 (1964) 19.

[24] W. Karminski, Z. Kulicki and Z. Stec, Chem. Stos., 13 (1969) 175 (CA 71; 101458b).

[25] E. Milchert, Pol. J. Appl. Chem., 32 (1988) 171.

[26] S. Baj, Frescenius' Z. Anal. Chem., 350 (1994) 159.

[27] S. Baj and Z. Kulicki, J. Chromatogr., 588 (1991) 33.

[28] J. Zawadiak, D. Gilner, Z. Kulicki and S. Baj, Analyst (London), 118 (1993) 1081.