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Thermal Stability and Polarographic Reduction of Peroxy Esters of *o*(*m*)-Carborane-1-carboxylic and Benzoic Acids

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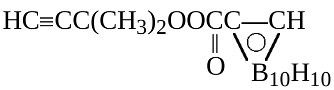
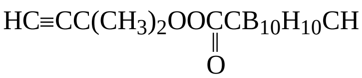
Abstract—The thermal stability of some peroxy esters of *o*(*m*)-carborane-1-carboxylic and benzoic acids (taken for comparison) was evaluated by thermal analysis. The polarographic reduction of these compounds on a mercury dropping electrode was studied. The parameters of the electrochemical reduction and thermal decomposition of the peroxy esters were analyzed.

Peroxy esters and diacyl peroxides derived from carboranecarboxylic acids, prepared in [1–4], exhibit a number of specific properties. Some of them can be used as initiators of styrene and methyl methacrylate polymerization, imparting to the resulting polymers enhanced resistance to thermal oxidative aging and to UV and γ-radiation [5–7]. However, the physicochemical properties of the majority of the synthesized carborane-containing peroxides have been studied insufficiently, which prevents determination of the optimal conditions of their application. The thermal stability of peroxy derivatives of *o*(*m*)-carboranes was estimated in the studies devoted to their synthesis [2–4]. We found no data on polarographic reduction of these compounds. At the same time, polarographic study of such peroxides allows prediction of their reactivity in various chemical transformations, including electrochemical processes.

In this work, we made a comparative estimation of the thermal stability of a series of peroxy esters derived from *o*(*m*)-carborane-1-carboxylic acids and studied their polarographic reduction on a mercury dropping electrode. As investigation objects we chose acetylenic carborane-containing peroxy esters and their saturated analogs: 3-methyl-3-*o*-carboranoylperoxy-1-butyne **I**, 3-methyl-3-*m*-carboranoylperoxy-1-butyne **II**, *tert*-butyl *o*-carborane-1-peroxycarboxylate **III**, and *tert*-butyl *m*-carborane-1-peroxycarboxylate **IV**. For comparison, we also studied peroxy esters derived from benzoic acid: *tert*-butyl peroxybenzoate **V**, 3-methyl-3-benzoylperoxy-1-butyne **VI**, and product of bromine addition across the triple bond in **VI**, 1,2-dibromo-3-methyl-3-benzoylperoxy-1-butene **VII** (*cis* isomer). To determine the polarographic activity of the carborane core under the similar conditions, we studied *o*-carborane (1,2-$C_2B_{10}H_{12}$, **VIII**) and *m*-carborane (1,7-$C_2B_{10}H_{12}$, **IX**). Acetylenic peroxy esters **I** and **II** [4], their saturated analogs [1], and peroxybenzoates **VI** [8] and **VII** [9] were prepared by published procedures. The samples of **I**–**VII** were 96–97% pure.


$HC\equiv CC(CH_3)_2OO\underset{\underset{O}{\|}}{C}\underset{B_{10}H_{10}}{C{-}CH}$

I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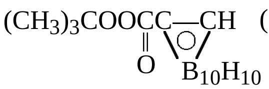
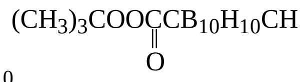
II


$(CH_3)_3COO\underset{\underset{O}{\|}}{C}\underset{B_{10}H_{10}}{C{-}CH}$

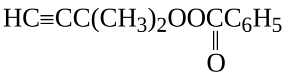
III


$(CH_3)_3COO\underset{\underset{O}{\|}}{C}CB_{10}H_{10}CH$

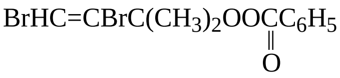
IV


$(CH_3)_3COO\underset{\underset{O}{\|}}{C}C_6H_5$

V


$HC\equiv CC(CH_3)_2OO\underset{\underset{O}{\|}}{C}C_6H_5$

VI


$BrHC{=}CBrC(CH_3)_2OO\underset{\underset{O}{\|}}{C}C_6H_5$

VII

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Table 1. Parameters of thermal stability of peroxy esters **I–VII**

Comp. no.	Decomposition step	Temperature, °C				Weight loss, %		Residue at 500°C, %
		melting	exoeffect maximum	$T_{o.d}$[a]	$T_{e.d}$[a]	in step	total	
I	First	95	136	118	150	55	68	26
	Second			179	230	13		
II	First	85	142	116	158	20	64	33
	Second			180	287	40		
	Third			342	470	4		
III	First	83	98	83	122	51	86	14
	Second			172	270	35		
IV	First	42	133	116	170	32	89	9
	Second			171	330	57		
V	First	–	149	94	170	62	86	10
	Second			180	355	24		
VI	First	–	128	96	155	75	94	3
	Second			190	345	19		
VII	First	69	130	105	139	25	89	1
	Second			139	165	17		
	Third			165	240	47		

[a] ($T_{o.d}$, $T_{e.d}$) Temperatures of the onset and end of the given decomposition step, respectively.

The thermal decomposition of the compounds in the bulk is accompanied by an exoeffect (Fig. 1) at a temperature specific for each peroxide (Table 1). The exothermic peaks in the DTA curves of **I**–**IV** and **VII** are preceded by endothermic peaks corresponding to the substance melting (Fig. 1). The TG curves of **I** and **III**–**VI** consist of two steps. The first step corresponds to vaporization of volatile thermal degradation products [10], and the second step, to removal of difficultly volatile products (Fig. 1, Table 1). The TG curves of **II** and **VII** consist of three steps. The exothermic peak of the DTA curves of the above compounds corresponds to the first step of the weight loss. The thermal effect in the DTA curve is due to reactions occurring in the crucible.

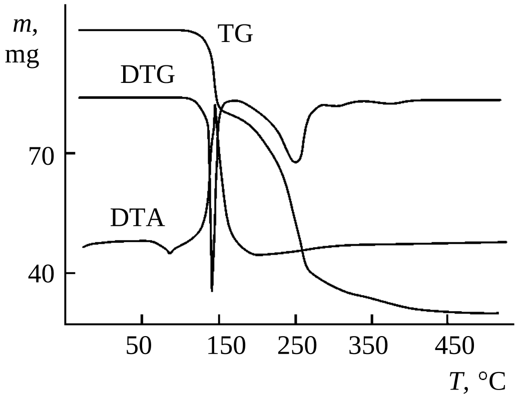

Fig. 1. TG, DTG, and DTA curves for peroxy ester **II**.

The thermal stability of peroxy esters **I**–**VII** was compared using the following parameters: temperature of the decomposition onset, course of decomposition, and weight loss (Table 1). The temperature of the thermolysis onset ($T_{o.d}$) was determined by averaging the DTG and DTA data [11, 12].

Liquid compounds **V** and **VI** show a 5–6% weight loss above 60°C, associated with their volatility and possible partial decomposition before the onset of the main exothermic effect [10]. The weight loss from the solids (**I**–**IV**, **VII**) starts only above ~100–110°C and amounts to 0.5–1.0%, which is probably also due to partial decomposition.

As seen from Table 1, the peroxy esters derived from *o*(*m*)-carborane-1-carboxylic acid, except **III**, are relatively stable compounds surpassing in the thermal stability the corresponding benzoic acid derivatives **V** and **VI**. The compounds start to decompose at a noticeable rate at 115–117°C ($T_{o.d}$ according to averaged DTG and DTA data), which is ~17–19°C higher compared to **V** and **VI**. The course of decomposition of carborane-containing peroxy esters **I** and **II** and acetylenic peroxybenzoate **VI** differs from that observed with *tert*-butyl peroxybenzoate **V**. The temperature interval of the first decomposition step spans

26–47°C for **I**–**IV** and **VI** but 76°C for **V**. The peak temperature for **V** (149°C) is also higher than for **I**, **II**, and **VI** (128–142°C). Acetylenic and saturated peroxy esters derived from *o*(*m*)-carborane-1-carboxylic acids also differ in the thermal stability. Compounds **I** and **II** have similar thermal stability, whereas *ortho* and met derivatives **III** and **IV** differ significantly: Compound **III** starts to decompose immediately after melting (83°C) or simultaneously with melting, i.e., at a 35°C lower temperature compared to **IV**. The appreciably lower stability of saturated peroxy derivatives of *o*-carboranes, compared to those of *m*-carboranes, in storage at 20–23°C, with rapid loss of available oxygen, was noted in [2–4]. The different thermal stability of saturated *o*- and *m*-carborane derivatives **III** and **IV** may be due to stronger electron-withdrawing properties of the *o*-carborane system compared to the *m*-carborane isomer [13], making the O–O bond more polar and thus less resistant to heat. However, in the case of ethynyl derivative **I**, the stronger electron-withdrawing effect of the *o*-carborane system does not cause an appreciable relative decrease in the thermal stability of **I** compared to **II**. Apparently, one of the factors preventing stronger polarization of the O–O bond under the influence of the carborane core in **I** may be steric factor. As shown in [4], according to the IR spectra, the carbonyl oxygen atom of the peroxy ester group can form an intermolecular hydrogen bond with the ethynyl proton. The hydrogen bonding is also suggested by increased melting points of **I** and especially **II**, as compared to their saturated analogs **III** and **IV**. The intermolecular association of the carbonyl group with the ethynyl proton was also noted for an acetylenic peroxy ester of benzoic acid [8]. However, this factor does not noticeably affect the thermal stability of **VI** compared to *tert*-butyl peroxybenzoate and that of acetylenic *m*-carborane ester **II** compared to its saturated analog **IV**. In the case of **I**, apparently, the effect of the carborane core on the O–O bond is more complex owing to different, compared to **III**, steric arrangement of the carborane core relative to the peroxy group. Table 1 shows that *ortho* and *meta* isomers **I**–**IV** differ also in the character of decomposition. The weight loss in the first decomposition step of *ortho* isomers **I** and **III** is considerably larger (51–55%) compared to *meta* isomers **II** and **IV** (20–32%). This fact suggests that the *o*- and *m*-carborane systems affect differently not only the decomposition mechanism, but also the nature of products formed from decomposition of the peroxy fragment in **I**–**IV**. Decomposition of *ortho* isomers **I** and **III** in the first step has a spontaneous, avalanche-like character and occurs with formation of a large amount of volatile products, as indicated by the jumpwise weight loss. It should be noted that the onset temperatures of the second steps of decomposition of the acetylenic peroxy esters (**I, II**) and their saturated analogs (**III, IV**) virtually coincide (Table 1). The total weight loss in the two steps is larger in the case of saturated esters **III** and **IV** (86–89%, against 60–65% for the acetylenic peroxy esters), suggesting formation of less volatile products in decomposition of **I** and **II**. Correspondingly, the residues at 500°C are larger in the case of **I** and **II** (26–33%, Table 1).

In the series of peroxybenzoates **V**–**VII**, the thermal stability somewhat increases in going from ethynyl derivative **VI** to its bromination product **VII** (Table 1).

With respect to the temperature of the decomposition onset, the peroxy esters under consideration can be ranked in the following order: **III** < **V** < **VI** < **VII** < **IV** ≅ **II** < **I**.

In view of the lack of data on the reactivity of **I**–**VII**, it seemed important to supplement the thermal analysis with a polarographic study, to obtain data that would allow prediction of the reactivity of these compounds in various chemical transformations.

We have studied **I**–**VII** polarographically in the concentration range $(0.5–5.0) \times 10^{-3}$ M.

Electrochemical reduction of **I**–**VII** in DMF [supporting electrolyte 0.1 M $(C_2H_5)_4NClO_4$] is described by polarograms of complex shapes (Figs. 2a, 2b), which is primarily due to their structural features, and also to possible associative processes in DMF solution in the presence of supporting electrolytes.

Detailed analysis of these curves shows that, despite differences in the curve shapes, voltammograms of these compounds have the main (second) wave corresponding to reduction of the O–O bond on mercury dropping electrode in the presence of $(C_2H_5)_4NClO_4$ (Fig. 2, Table 2). The limiting currents (I_{lim}) of the main reduction waves of **I**–**VII** have the diffusion nature, as suggested by the concentration dependences (Fig. 3), and at the depolarizer concentration (C_{dep}) of 2.50×10^{-3} M they are within 4.0–8.0 μA (Table 2). This is also confirmed by the results of experiments on studying how the limiting currents of peroxy ester reduction depend on the mercury column height. The dependences of the reduction currents of **I**–**IV** on the $(C_2H_5)_4NClO_4$ concentration show that the diffusion character of the limiting currents of the main wave is preserved. The values of $I_{\text{lim}} = f(C_{\text{dep}})$ for **II** and **IV**, in contrast to those for **I** and **III**, are virtually independent of the supporting electrolyte concentration (Fig. 4). This fact suggests higher sensitivity of the electrochemical reaction involving **I** and **III** on mercury dropping electrode to both concentration and nature of the supporting electrolyte.

Table 2. Parameters of electrochemical reduction of peroxy esters **I–VII** (C_{dep} 2.5×10^{-3} M). Supporting electrolyte 0.1 M $(C_2H_5)_4NClO_4$ in DMF[a]

Comp. no.	First wave			Second (main) wave			Third wave		
	$-E_{1/2}$, V	I_{lim}, μA	*b*, mV	$-E_{1/2}$, V	I_{lim}, μA	*b*, mV	$-E_{1/2}$, V	I_{lim}, μA	*b*, mV
I	–	–	–	1.32	4.50	94	1.78	3.05	222
II	0.32	0.75	128	0.94	4.70	227	–	–	–
III	1.18	2.90	111	1.42	5.00	77	1.84	2.70	200
IV	0.60	1.30	222	1.10	6.60	214	–	–	–
V	–	–	–	0.92	7.55	127	–	–	–
VI	0.90	3.25	167	1.28	4.25	80	–	–	–
VII	0.61	2.70	98	1.07	5.20	188	1.76	3.00	64

[a] For parameters of the fourth reduction wave observed with **I** and **IV**, see text.

The first wave in the polarograms of **II**–**IV** has a pronounced adsorption nature: Its height and shape are virtually independent of the depolarizer (Fig. 3) and supporting electrolyte $[(C_2H_5)_4NClO_4]$ concentrations, with I_{lim} being about 0.75–2.90 μA.

An increase in the radius of the supporting electrolyte cation in going from $(C_2H_5)_4NClO_4$ to $(C_4H_9)_4N \cdot ClO_4$ favors solubilization of the depolarizer molecules in the near-electrode layer. As a result, the depolarizer concentration near the electrode grows, causing the cathodic currents of the first wave to increase, with $E_{1/2}$ of reduction of **II** remaining the same. The extent of the process irreversibility decreases (*b* 98 mV), indirectly suggesting simpler mechanism of electrochemical reduction of **II** with $(C_4H_9)_4NClO_4$ supporting electrolyte. For the second wave, $E_{1/2}$ shifts toward anodic region to –0.76 V. Our results indirectly confirm that electrochemical reduction of carborane-containing peroxy esters on mercury dropping electrode occurs by two parallel reactions described in [14] and involving homolytic and heterolytic cleavage of the O–O bond.

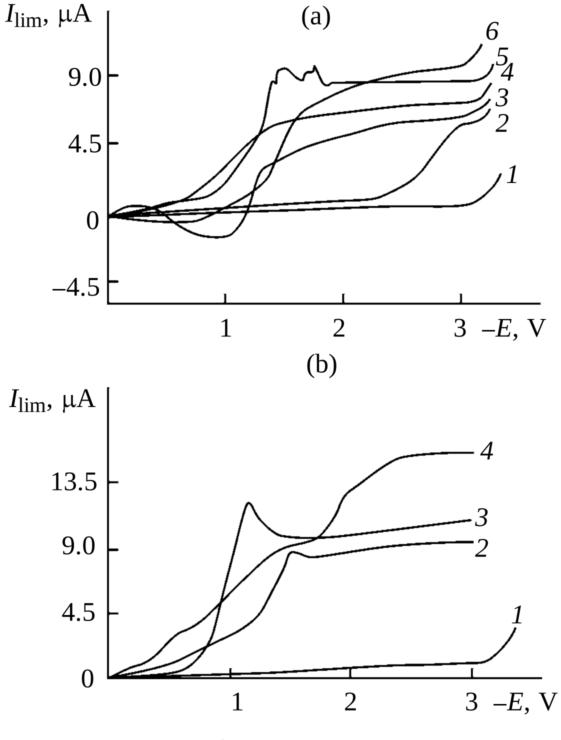

Fig. 2. General view of the polarograms. (a) Carborane-containing peroxy esters and *o*-carborane: (*2*) **VIII**, (*3*) **I**, (*4*) **II**, (*5*) **IV**, and (*6*) **III**. (b) Peroxybenzoic acid esters: (*2*) **VI**, (*3*) **V**, and (*4*) **VII**. C_{dep} 2.5×10^{-3} M. (*1*) Supporting electrolyte [0.1 M $(C_2H_5)_4NClO_4$ in DMF] without depolarizer added.

Electrochemical reduction of *meta* derivatives of carborane-1-carboxylic acid **II** and **IV** with 0.1 M $(C_2H_5)_4NClO_4$ in DMF as supporting electrolyte occurs more readily, i.e., at lower half-wave potentials and is irreversible to a greater extent as compared to reduction of the *ortho* derivatives **I** and **III** (Table 2). Peroxy esters **I** and **II** containing an ethynyl fragment are less resistant to electrochemical reduction as compared to **III** and **IV**, which may be due to increased electrophilicity of the peroxides containing the triple bond.

The reduction of **I** with 0.1 M $(C_4H_9)_4NClO_4$ in DMF as supporting electrolyte is described by a complex polarogram consisting of three waves with the $E_{1/2}$ values for the first, second, and third waves of –1.20, –2.16, and –2.64 V, respectively (Fig. 5). The half-wave potential of the first wave for **I** with 0.1 M $(C_4H_9)_4NClO_4$ supporting electrolyte virtually coincides with $E_{1/2}$ for the first wave of the voltammogram of **I** obtained with 0.1 M $(C_2H_5)_4NClO_4$ supporting electrolyte (Table 2) and corresponds to reduction of the O–O bond. The second ($E_{1/2}$ –2.16 V) and

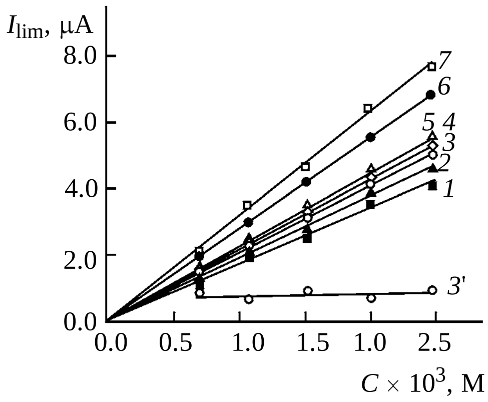

Fig. 3. Concentration dependences of the limiting reduction currents: (*1*–*7*) compounds **I**–**VII**, main wave; (*3*') compound **II**, first wave. Compound: (*1*) **VI**, (*2*) **I**, (*3*) **II**, (*4*) **III**, (*5*) **VII**, (*6*) **IV**, and (*7*) **V**.

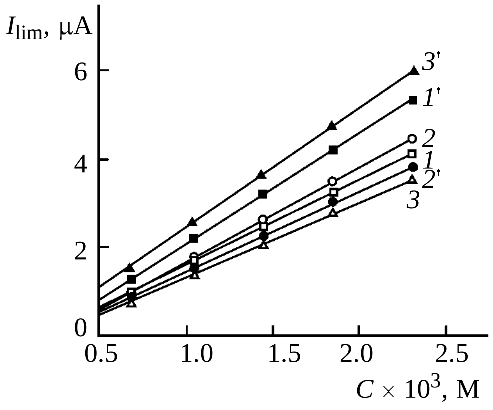

Fig. 4. Influence of the supporting electrolyte [(*1*–*3*) $(C_2H_5)_4NClO_4$ and (*1*'–*3*') $(C_4H_9)_4NClO_4$] concentration [(*1, 1*') 0.01, (*2, 2*') 0.10, and (*3, 3*') 0.3 M] on the concentration dependence of the limiting current of reduction of **III** (main wave).

third ($E_{1/2}$ –2.64 V) waves apparently correspond to electrochemical reduction of the *o*-carborane core in 3-methyl-3-*o*-carboranoylperoxy-1-butyne **I**. As the concentrations of **I** and **III** [with $(C_4H_5)_9NClO_4$ in DMF as supporting electrolyte] are increased, the shape of the voltammograms in the examined concentration range does not change. Changes become noticeable with $(C_2H_5)_4NClO_4$ supporting electrolyte on reaching C_{dep} 2.00×10^{-3} M. The electrochemical reduction of **I** with $(C_4H_9)_4NClO_4$ supporting electrolyte is more reversible than with $(C_2H_5)_4NClO_4$.

In electrochemical reduction of **I** and **III** on mercury dropping electrode with 0.1 M $(C_2H_5)_4NClO_4$ in DMF as supporting electrolyte, an increase in the depolarizer concentration is accompanied by appearance of deflections [15] in the polarographic curves in the potential range from –0.25 to –1.50 V for **I** and from –0.10 to –1.20 V for **III** (Fig. 2a, curves *3*, *6*). The current somewhat grows at the beginning of the electrochemical process; then, on reaching the adsorption potential, it decreases owing to suppression of the motions of the mercury surface and inhibition of the electrochemical reduction of **I** and **III** proper; after passing a minimum, the current starts to grow again. These trends are due to the surface activity of *o*-carborane derivatives **I** and **III**, manifested in the adsorption (E from 0.4 to –0.5 V) and desorption ($E \geq -0.5$ V) potentials [16, 17].

The deflections in the polarograms of **I** appear on reaching C_{dep} 0.6×10^{-3} M, and with **III** they appear only at C_{dep} 1.2×10^{-3} M. The deflections become stronger as the depolarizer concentration is increased. With increasing concentration of supporting electrolyte, the deflections become somewhat less pronounced, the half-wave potentials shift to the anodic region, and the main wave of electrochemical reduction of **I** and **III** on mercury dropping electrode becomes more irreversible. With $(C_4H_9)_4NClO_4$ supporting electrolyte, no deflections are observed. This effect is due to adsorption–desorption processes in the electrical double layer on the surface of the mercury dropping electrode, involving both tetraethylammonium ions and molecules of *o*-carborane-1-carboxylic acid derivatives **I** and **III** [16, 17]. It should be noted also that, in reduction of ethynyl-substituted peroxy ester **I**, the deflections are larger compared to **III**. This may be due to additional effect of the ethynyl group on the adsorption–desorption processes in the electrical double layer.

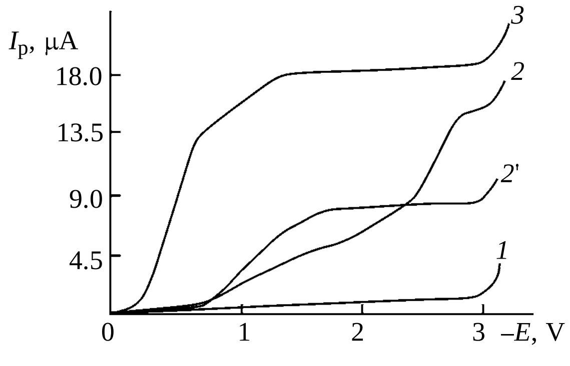

Fig. 5. Polarograms of peroxides: (*1*) supporting electrolyte, (*2*) **I**, and (*3*) **II**. Supporting electrolyte 0.1 M $(C_4H_9)_4NClO_4$ in DMF. (*2*') compound **I** with 0.3 M $(C_2H_5)_4NClO_4$ in DMF as supporting electrolyte. C_{dep} 2.50×10^{-3} M.

With the aim to study the electrochemical activity of the carborane core, we performed polarographic experiments with *o*- and *m*-carboranes **VIII** and **IX** under the same conditions as those used for **I**–**IV** [supporting electrolyte 0.1 M $(C_2H_5)_4NClO_4$]. The experiments have shown that compound **IX** is not reduced on mercury dropping electrode, in agreement with published data [18]. In contrast to *m*-carborane **IX**, *o*-carborane **VIII** is reduced in the far cathodic region. Its voltammogram consists of two waves at a depolarizer concentration of 0.70×10^{-3} M (Fig. 2a). The value of $E_{1/2}$ –2.56 V for the first wave is consistent with data from [16]. At $E_{1/2}$ –2.92 V, the second, more reversible (*b* 144 mV) wave is observed. As the depolarizer concentration is increased above 0.70×10^{-3} M, the waves of electrochemical reduction of **VIII** change in character; in particular, the second wave (*b* 136 mV) becomes more reversible than the first wave (*b* 160 mV). For both the first and the second waves, $E_{1/2}$ shifts toward anodic region, reaching –2.50 and –2.90 V, respectively. The concentration dependence of the limiting reduction currents of **VIII** is linear, suggesting their diffusion character. The presence of *o*-carborane **VIII** in a solution of 3-methyl-3-*o*-carboranoylperoxy-1-butyne **I** does not affect the shape of the polarographic wave of **I** and the parameters of its electrochemical reduction, whereas the two-step wave of **VIII** transforms into a one-step, more reversible wave with $E_{1/2}$ –2/70 V.

Analysis of the polarograms of 3-methyl-3-*o*-carboranoylperoxy-1-butyne **I** recorded with 0.1 M $(C_4H_9)_4NClO_4$ supporting electrolyte shows that the first wave ($E_{1/2}$ –1.20 V) corresponds to the reduction of the O–O group. The second ($E_{1/2}$ –1.50 V) and third ($E_{1/2}$ –2.00 V) waves apparently correspond to reduction of the *o*-carborane fragment of **I**. In the case of **III**, the second (main) wave with $E_{1/2}$ –1.42 V corresponds to the electrochemical reduction of the O–O group, and the third wave ($E_{1/2}$ –1.84 V), to reduction of the *o*-carborane fragment.

These studies show that the *o*-carborane fragment present in the molecules of **I** and **III** is electrochemically active and is reduced in the far cathodic region, affecting the shape and parameters of the main reduction wave of the O–O group.

Since the carborane core is a quasiaromatic system, we studied the electrochemical activity of *tert*-butyl peroxybenzoate **V** and related unsaturated derivatives **VI** and **VII** with the aim to compare their reactivities on mercury dropping electrode. Peroxy esters **V**–**VII** are polarographically active and are reduced in the potential range from –0.6 to –2.00 V (Fig. 2b).

There is no common opinion on the nature of the first reduction wave of peroxy esters (whether it corresponds to reduction of peroxy ester proper or its decomposition products) [14, 19].

Electrochemical reduction of **V** (C_{dep} 5.0×10^{-4} M) with 0.1 M $(C_2H_5)_4NClO_4$ in DMF as supporting electrolyte is described by a two-electron irreversible (*b* 167 mV) wave with $E_{1/2}$ –0.90 V. As the depolarizer concentration is increased, the polarographic wave becomes somewhat distorted owing to appearance of an adsorption maximum at C_{dep} 1.00×10^{-3} M, whose height is proportional to the depolarizer concentration and decreases with increasing supporting electrolyte concentration. In so doing, the half-wave potential remains unchanged, –0.92 V (Table 2). The parameters of the electrochemical reduction of **V** are virtually independent of the concentration and nature of the supporting electrolyte. The first wave in the polarogram of **V** is absent, as in the case of **I**, and the main wave corresponds to reduction of the O–O group; its limiting currents have the diffusion nature (Fig. 3, curve *7*).

The presence of adsorption maxima distorting the main wave is also characteristic of *m*-carborane-1-carboxylic acid derivative **IV** and 3-methyl-3-benzoylperoxy-1-butyne **VI** (Figs. 2a, 2b). These maxima appear at C_{dep} 1.00×10^{-4} M for **IV** and 1.00×10^{-3} M for **VI**. Their heights are virtually independent of the concentrations of **IV** and **VI**.

The limiting currents of the first wave of electrochemical reduction of **VI**, in contrast to those observed with **II**–**IV** and **VII** (Fig. 3, Table 2), depend on the depolarizer concentration and have the diffusion nature; the process corresponding to these currents is more reversible in the case of **VI** (*b* is lower compared to **II**–**IV** and **VII**).

The polarogram of 1,2-dibromo-3-methyl-3-benzoylperoxy-1-butene **VII** additionally contains two waves with $E_{1/2}$ –1.76 and –2.00 V (Fig. 2b). These waves are apparently due to electrochemical reduction of bromine and vinyl group ($E_{1/2}$ –2.00 V), which is known to occur in this potential range [20].

The observed cathodic shift of $E_{1/2}$ of the main reduction wave of peroxybenzoates **VI** and **VII**, compared to **V** (Table 2, Fig. 2b), is attributable, along with other factors, to an increase in the electrophilicity and polarizability of the molecules of these compounds in the order **V** < **VII** < **VI**, owing to the presence of the ethynyl (in **VI**) or dibromoalkenyl (in **VII**) fragment.

Thus, the chemical structure of carborane-containing peroxy esters (in particular, the presence of functional groups in hydrocarbon substituents) is the major factor governing their electrochemcial activity and thermal stability.

EXPERIMENTAL

Thermal decomposition of peroxy esters **I**–**VII** was studied on a Paulik–Paulik–Erdey Q-1500D derivatograph in quartz crucibles in air in the temperature range from 20 to 500°C at a linear heating rate of 10 $\mathrm{deg\,min^{-1}}$. The peroxide sample weights were 100 mg.

The polarographic study was performed as described previously [21]. Voltammograms were recorded with a PU-1 polarograph using a two-electrode Novak cell. As working electrode we used a mercury dropping electrode with the dropping period τ 5.89 s and capillary characteristic $m^{2/3}\tau^{1/6} = 1.59\ \mathrm{mg}^{2/3}\ \mathrm{s}^{-1/2}$ (m is the weight of mercury flowing out of the capillary of the dropping electrode in unit time) in the supporting electrolyte solution at the mercury column height of 0.37 m and open circuit. The solution was deoxygenated by argon bubbling. As supporting electrolytes we used solutions of polarographic grade $(C_2H_5)_4NClO_4$ and $(C_4H_9)_4NClO_4$ in DMF.

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