Russian Journal of General Chemistry, Vol. 74, No. 7, 2004, pp. 1031–1037. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 7, 2004, pp. 1119–1125.
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Thermal Stability of Peroxyalkynes

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Received June 24, 2002

Abstract—The thermal stability of mono- and disubstituted peroxyalkynes was compared. The reaction order and the apparent activation energy for the first step of decomposition of the peroxides were determined. The strength of the O–O bond in 3-*tert*-alkyl(cycloalkyl, aralkyl)peroxy-3-methyl-1-butynes and 2-*tert*-alkylperoxy-2-methyl-2-alkynes was estimated.

In [1] we estimated derivatographically the thermal stability of functionally substituted peroxyalkynes: tertiary mono- and polycyclic peroxy alcohols and their derivatives.

In this work we studied derivatographically [2] the thermal stability of mono- and disubstituted peroxyalkynes, 3-*tert*-alkyl(cycloalkyl, aralkyl)peroxy-3-methyl-1-butynes **Ia**–**Id** [3] and 1-deutero-3-methyl-3-(2-cyclohexyl-2-propylperoxy)-1-butyne **Ie** [4], of oprganosilicon peroxyalkynes, 3-*tert*-alkyl(cycloalkyl, aralkyl)peroxy-3-methyl-1-trimethyl(phenyl)silyl-1-butynes **IIa**–**IIc** and **IIIa**–**IIIg** [5], and of long-chain peroxyalkynes, 2-*tert*-alkylperoxy-2-methyl-3-alkynes **IVa**–**IVu** [6]. Among diperoxides, we studied 2,5-di-*tert*-alkyl(alkynyl)peroxy-2,5-dimethyl-3-hexynes (-hexanes) **Va**–**Vc** and **VIa** [3, 7], organosilicon diperoxides, 2-*tert*-butylperoxy(1-trimethylsilylalkynylperoxy)-2,5-dimethyl-5-[1-triphenyl(methyl)silylalkynylperoxy]-3-hexynes **Vd** and **Ve** and dimethyldi-[3-methyl-3-*tert*-alkyl(cycloalkyl)peroxy]silanes **VIIIa**–**VIIId** [5], a diiodo-substitted diperoxide, 2,5-dimethyl-2,5-di(1-iodoalkynylperoxy)hexane **VIb** [8], and diacetylenic diperoxides, 2-*tert*-alkylperoxy-7-*tert*-alkyl(aralkyl)peroxy-2,7-dimethyl-3,5-octadiynes **VIIa**–**VIIc** [9, 10]. For comparison, we studied dicumyl peroxide **IX**.

$RC{\equiv}CCMe_2O_2R'$

Ia–Ie, IIa–IIc, IIIa–IIIg, IVa–IVu, Va–Ve, VIa, VIb, VIIa–VIIc, VIIIa–VIIId, Xa–Xc

I, R = H, R' = $CMe_2(CH_2)_4Me$ (**a**), Me_2C-*cyclo*-C_6H_{11} (**b**); CMe_2Ph (**c**), CPh_3 (**d**); R = D, R' = Me_2C-*cyclo*-C_6H_{11} (**e**); **II**, R = $SiMe_3$, R' = $CMe_2(CH_2)_4Me$ (**a**), Me_2C-*cyclo*-C_6H_{11} (**b**), CMe_2Ph (**c**); **III**, R = $SiPh_3$, R' = CMe_3 (**a**), CMe_2Et (**b**), CMe_2Pr (**c**), $CMe_2(CH_2)_4Me$ (**d**), Me_2C-*cyclo*-C_6H_{11} (**e**), CMe_2Ph (**f**), CPh_3 (**g**); **IV**, R = $(CH_2)_xMe$, R' = CMe_3 (**a, d, g, j, m, p, s**), CMe_2Et (**b, e, h, k, n, q, t**), CMe_2Pr (**c, f, i, l, o, r, u**), x = 3 (**a**–**c**), 5 (**d**–**f**), 9 (**g**–**i**), 11 (**l**–**l**), 14 (**m**–**o**), 15 (**p**–**r**), 17 (**s**–**u**); **V**, R = CMe_2O_2X, X = R' = $CMe_2C{\equiv}CH$ (**a**), CMe_3 (**b**); X = $CMe_2C{\equiv}CH$, R' = CMe_3 (**c**); X = $CMe_2C{\equiv}CSiPh_3$, R' = CMe_3 (**d**); X = R' = $CMe_2C{\equiv}CSiMe_3$ (**e**); **VI**, R = N, R' = $CMe_2(CH_2)_2CMe_2 \cdot O_2CMe_2C{\equiv}CX$, X = H (**a**), X = R = I (**b**); **VII**, R = $C{\equiv}CCMe_2O_2X$, X = R' = CMe_3 (**a**); X = $CMe_2(CH_2)_4Me$, R' = CMe_3 (**b**); X = CMe_2Ph, R' = CMe_3 (**c**); **VIII**, R = $SiMe_2C{\equiv}CCMe_2O_2X$, X = R' = CMe_3 (**a**), CMe_2Et (**b**), CMe_2Pr (**c**), Me_2C-*cyclo*-C_6H_{11} (**d**); **X**, R = H, R' = CMe_3 (**a**), CMe_2Et (**b**), CMe_2Pr (**c**).

The thermal stability of mono- and disubstituted peroxyalkynes **I**–**VIII** and peroxide **IX** was characterized by the temperature of decomposition onset (T_o), decomposition pattern, and weight loss (Table 1). Depending on the volatility and stability of the decomposition products, the DTG and TG curves show different numbers of steps of the weight loss: one step in the case of **IIIa**, **IVa**–**IVc**, and **VIb**; two steps in the case of **Ia, Ic, IIa**–**IIc, IVd**–**IVi, Va**–**Ve, VIa, VIIa**–**VIIc, VIIIb, VIIId**, and **IX**; three in the case of **Ib, Id, Ie, IIIb**–**IIId, IVo**–**IVu, VIIb, VIIIa**, and **VIIIc**; four in the case of **IIId**–**IIIg** and **IVk**–**IVn**; and five in the case of **IVj**.

In the first step (165–220°C), peroxides **I**–**IX** decompose with a pronounced exothermic effect (DTA curves), and the other steps are not accompanied by significant thermal effects and largely correspond to removal of volatile decomposition products. The DTA curves show pronounced exothermic peaks characteristic of definite types of peroxyalkynes (see figure; Table 1). The exothermic peaks in the DTA curves of solid compounds **Ic, Id, IIIa, IIIe, IIIg, VIIa**–**VIIc**,

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Table 1. Thermal stability (T_o, T_e, T_m, °C; Δm, %) of peroxides **I**–**IX** (first decomposition step)

Comp. no	DTG			TG, Δm	DTA, exo peak		n	E_a, kJ mol^{-1}
	T_o	T_e	T_{max}		T_o	T_{max}		
Ia	130	197	158	76	132	164	1.67	148
Ib	108	165	145	50	107	148	1.48	116
Ic^b	127	175	154	47	128	155	1.45	160
Ic^c	124	205	157	76	124	158	1.41	159
Ic^d	125	220	159	71	125	160	1.87	–
Ic^e	125	180	158	56	123	158	1.42	151
Id	110	166	149	51	108	151	1.40	118
Ie	135	167	156	10.5	128	159	1.60	156
IIa	138	210	177	76	138	177	1.36	138
IIb	122	205	168	75	122	170	1.30	122
IIc	130	203	169	69	129	168	1.38	150
IIIa	146	205	172	17	143	177	1.20	142
IIIb	142	200	178	15.5	140	180	1.24	132
IIIc	147	208	182	15.5	141	188	1.26	129
IIId	151	215	182	15	139	184	1.26	131
IIIe	132	205	175	23	127	177	1.22	123
IIIf	145	208	186	18	141	188	1.26	154
IIIg^f	150	206	172	3	–	–	–	–
IVa	137	195	165	83	138	179	1.10	137
IVb	135	200	170	85	134	180	1.16	132
IVc	134	200	168	83	135	178	1.17	131
IVd	138	205	167	74	138	175	1.24	138
IVe	136	205	166	68	137	176	1.18	133
IVf	138	210	169	71	139	179	1.26	131
IVg	140	197	179	41	140	182	1.26	140
IVh	138	200	177	45	139	182	1.26	134
IVi	136	200	178	45	137	181	1.19	132
IVj	138	195	179	32	140	181	1.16	139
IVk	135	197	176	34	136	179	1.20	133
IVl	135	195	175	33	137	178	1.13	134
IVm	140	195	178	30	142	180	1.13	144
IVn	139	215	188	30	140	190	1.26	136
IVo	140	195	180	25	141	182	1.22	137
IVp	146	201	185	21	147	187	1.26	142
IVq	140	205	186	15.5	141	187	1.15	133
IVr	140	198	178	19	140	180	1.14	135
IVs	148	205	185	20	148	190	1.24	144
IVt	142	200	177	17	142	182	1.18	135
IVu	140	197	180	22.5	141	184	1.13	138
Va	103	198	162	61	102	162	1.16	90
Vb	116	187	162	87	116	164	1.14	109
Vc	110	195	159	72	112	160	1.36	110
Vd	132	216	182	63	132	182	1.20	113
Ve	145	205	185	25	145	186	1.36	161
VIa	105	185	153	60	105	155	1.35	101
VIb	123	184	162	65	123	162	1.52	160
VIIa	102	170	146	48	102	148	1.53	150
VIIb	112	182	155	43	110	157	1.52	152
VIIc	110	185	146	52	110	146	1.66	178
VIIIa	137	207	179	55	137	179	1.44	156
VIIIb	134	200	172	50	134	175	1.49	152
VIIIc	131	198	170	45	131	172	1.54	158
VIIId	124	205	165	49	124	168	1.43	144
IX^b	130	175	164	42	131	164	1.10	152
IX^c	127	177	162	43	127	163	1.16	154
IX^d	128	212	165	62	128	166	1.26	157

[a] (T_o, T_{max}, T_e) Temperatures of the onset, maximum, and end of decomposition, respectively; (Δm) weight loss. [b] 5 deg min^{-1}, Ar. [c] 7 deg min^{-1}, Ar. [d] 15 deg min^{-1}, Ar. [e] 7 deg min^{-1}, air. [f] T_m (150°C) = T_o. [g] 10 deg min^{-1}, Ar.

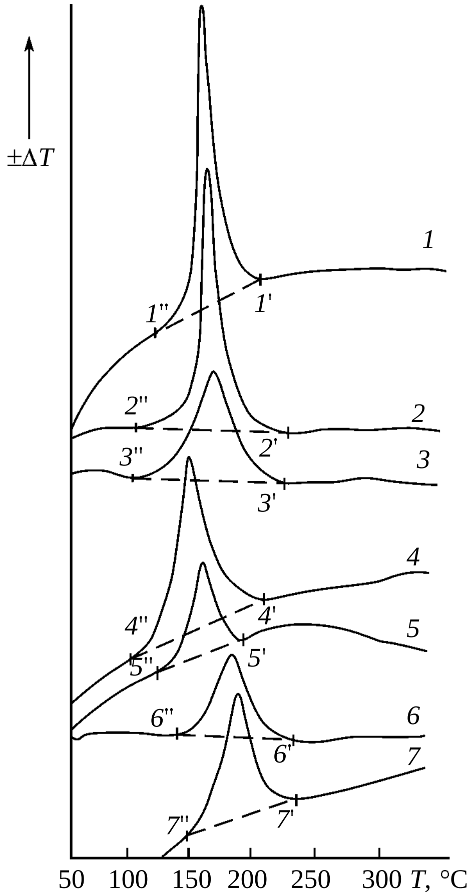
and **IX** are preceded by endothermic peaks corresponding to melting of these compounds.

The T_o values were determined from the DTG and DTA curves as the interception points of the peaks with the baseline (for DTA curves, see figure). For relatively volatile compounds **Ia, IIa, IVa**–**IVd, Vb**, and **Vc**, the T_o(DTG) values were estimated according to [11]. For peroxyalkyne **Id** with triphenylmethylperoxy group and in the series of disubstituted peroxyalkynes with the triphenylsilyl group at the C≡C bond (**IIIc**–**IIIf**), T_o(DTG) is 5–10°C higher than T_o(DTA), which is due to formation of low-volatile and difficultly removable decomposition products. For comparative evaluation of the thermal stability of peroxides **I**–**IX**, we used the parameter T_o(DTA), which is virtually independent of the heating rate and atmosphere (peroxides **Ic**, **IX**, Table 1). From the parameters of the exothermic peak in the DTA curves, we calculated the order n and activation energy E_a of thermal decomposition [12]. To obtain comparable results, thermolysis of **I**–**IX** was performed under similar conditions at a heating rate of 7 deg min^{-1}.

As seen from Table 1, mono- and disubstituted peroxyalkynes **I**–**VIII** are relatively stable and start to decompose at a noticeable rate at 102–148°C depending on the structure. Monosubstituted peroxyalkynes **Ia**–**Ie** are stable up to 107–132°C (Table 1), with the compounds containing *tert*-alkyl(aralkyl)peroxy groups (**Ia, Ic, Id**) being comparable in the thermal stability (T_o 124–132°C) with peroxide **IX** (T_o

127°C). Peroxyalkynes containing cycloalkylperoxy groups (**Ib, Ie**) are less stable (T_o 107, 108°C) than compound **Ia** containing *tert*-alkylperoxy groups. This may be de to lower mobility of the atoms of the cycloalkyl radical as compared to atoms of the alkyl radicals, which hinders redistribution of excess heat within the molecule because of higher energy barriers and steric hindrance in the case of the cyclohexane ring [13]. The pattern of decomposition of monosubstituted peroxyalkynes **Ia**–**Ie** differs from that of **IX**. The calculated order of thermal decomposition of **IX** is close to unity (n 1.16 at 7 deg min^{-1}), with E_a 154 kJ mol^{-1} (Table 1), which is consistent with published data on E_a of thermolysis of **IX** in solutions (138–167.4 kJ mol^{-1}) [14]. For monosubstituted peroxyalkynes **Ia**–**Ie**, n noticeably differs from unity (1.40–1.67), which is due to different contribution of the induced decomposition. For peroxides **Ia**, **Ic**, and **Id**, E_a is 148–159 kJ mol^{-1}, and for cycloalkylperoxides **Ib** and **Ie**, 116 and 118 kJ mol^{-1}, respectively. Replacement of the ethynyl hydrogen atom in peroxyalkynes **Ia**–**Ie** with the trimethyl(phenyl)silyl group not only increases T_o(DTA) to 122–143°C, but also alters the pattern of decomposition of disubstituted peroxyalkynes **IIa**–**IIc** and **IIId**–**IIIf** (Table 1). Compounds **IIa**–**IIc** with the trimethylsilyl group have n within 1.30–1.38, and for the related compounds **IIId**–**IIIf** with the triphenylsilyl group n is 1.22–1.26. As in the case of monosubstituted peroxyalkynes **Ib** and **Ie**, disubstituted peroxyalkynes with cycloalkylperoxy groups (**IIb, IIIe**) decompose at lower temperatures (122, 127°C) and with lower E_a (122, 123 kJ mol^{-1}) than the related compounds with *tert*-alkylperoxy groups (**IIa, IIIa**–**IIId**) (E_a 129–142 kJ mol^{-1}).

Disubstituted long-chain peroxyalkynes **IVa**–**IVu** (Table 1) also show higher thermal stability than monosubstituted peroxyalkynes **Ia**–**Ie**. They start to decompose at a noticeable rate at 134–148°C. For peroxides **IVa**–**IVu**, E_a is 131–144 kJ mol^{-1}, and n is 1.10–1.26. In this series, the thermal stability somewhat grows with increasing length of the alkyl substituent at the triple bond. Peroxyalkynes with hexadecyl (**IVp**–**IVr**) and octadecyl (**IVs**–**IVu**) substituents have T_o 140–148°C, which is 5–10°C higher than T_o of related compounds with a shorter length of the alkyl substituent. Compounds with *tert*-butylperoxy groups decompose with higher E_a (by up to ~9 kJ mol^{-1}) than the related compounds with *tert*-pentylperoxy (**IVb, IVe, IVh, IVk, IVn, IVq, IVt**) and 2-methyl-2-pentylperoxy groups (**IVc, IVf, IVi, IVl, IVo, IVr, IVu**), which is consistent with the results of quantum-chemical calculations of functionally substituted peroxyalkynes [15] and with the results of [16].



DTA curves of peroxides (*1*) **Ic**, (*2*) **VIa**, (*3*) **Va**, (*4*) **Ib**, (*5*) **IX**, (*6*) **IIIa**, and (*7*) **IVs**. Interception points: (*1*'–*7*') for T_e and (*1*''–*7*'') for T_o. Dashed lines: baselines for determining n and E_a.

Changes in the decomposition pattern that occur in going from disubstituted peroxyalkynes with one peroxy group (**II**–**IV**) to compounds with two peroxy groups (**V**–**VIII**) are also due to mutual influence of the peroxy groups in the molecule. Diperoxides **V**–**VIII** decompose with E_a from 90 to 178 kJ mol^{-1} and n 1.14–1.66 depending on the structure (Table 1). *tert*-Alkyl(alkynyl) diperoxides **Va**–**Vc** and **VIa** are less stable thermally than monoperoxides **Ia** and **IVa**–**IVu** (Table 1) and start to decompose at a noticeable rate at 102–116°C, which is ~30°C lower than T_o of the monoperoxides. In the series of diperoxides **Va**–**Vc** and **VIa**, the thermolysis parameters especially strongly depend on the structure. In particular, in going from diperoxide **Va** with two alkylperoxy groups to its analog **VIa** containing no triple bond in the middle part of the molecule, n increases from 1.16 to 1.35, and E_a, from 90 to 101 kJ mol^{-1}; the exothermic effect (DTA) in decomposition of the saturated analog **VIa** is more significant. Changes in the thermal decomposition pattern are also observed in going from acetylenic diperoxide **Vb** containing two *tert*-butylperoxy groups to its diacetylenic analog **VIIa**. Diperoxide **Vb** starts to decompose at 116°C, with n 1.14 and E_a 109 kJ mol^{-1}; diacetylenic diperoxide **VIIa** starts to decompose even at 102°C, with n 1.53 and E_a 150 kJ mol^{-1}, which is due to increased contribution of induced decomposition. In the series of diacetylenic diperoxides **VIIa**–**VIIc**, compounds with different alklperoxy (**VIIb**) or alkyl- and aralkylperoxy (**VIIc**) groups start to decompose at higher temperatures (110, 112°C) compared to compound **VIIa** with two equal alkylperoxy groups. Diacetylenic peroxides **VIIa**–**VIIc**, in contrast to acetylenic diperoxide **Vb**, spontaneously decompose in air even at 130°C. Similar to monosubstituted peroxyalkynes **Ia**–**Ic**, replacement of the ethynyl hydrogen atom in diperoxide **Va** with trimethylsilyl groups and in diperoxide **VIa** with the iodine atom noticeably increases the thermal stability of **Vd** and **VIb** (by 42 and 18°C, respectively) and affects the kinetic parameters of the decomposition (Table 1).

Organosilicon diperoxides **VIIIa**–**VIIId** exhibit enhanced thermal stability and start to decompose only at 124–137°C. In their series, as in the case of organosilicon monoperoxides **IIa**, **IIb**, and **IIIa**–**IIIe**, compounds **VIIIa**–**VIIIc** containing alkylperoxy groups have somewhat higher T_o (131–137°C) and E_a (152–158 kJ mol^{-1}, n 1.44–1.54) than compound **VIIId** with cycloalkylperoxy groups (T_o 124°C, E_a 144 kJ mol^{-1}) (Table 1).

We attempted to determine E_a of thermal decomposition of certain nonvolatile disubstituted peroxyalkynes with the reaction order close to unity by processing of the TG curves according to Broido [12]. This method is used in derivatography for substances decomposing in a narrow temperature range by a first-order reaction. In the series of long-chain peroxyalkynes **IVs**–**IVu**, E_a of thermal decomposition calculated by the Broido method (TG) [17] is 143–151 kJ mol^{-1}, which is comparable with the values determined by DTA, E_a 135–144 kJ mol^{-1} (Table 1).

Presumably, decomposition of peroxides **I**–**VIII** in the first step (up to 165–220°C) occurs mainly as cleavage of the O–O bond. In decomposition of long-chain peroxyalkynes **IVs**–**IVu** with the octadecyl radical at the triple bond, the nonvolatile residue from the first step of decomposition (up to 200–205°C) contains no peroxy products (TLC data on Silufol UV-254 plates; ^{1}H NMR and IR spectra). The weight loss, ~20% for **IVs**, ~17% for **IVt**, and 22% for **IVu**, corresponds to removal of volatile products formed in the decomposition and in secondary reactions of tertiary alkoxy radicals generated by homolytic cleavage of peroxyalkynes **IVs**–**IVu**. The ^{1}H NMR and IR spectra of the decomposition products of **IVs**–**IVu** suggest the absence of alkylperoxy groups with preservation of the other molecular fragments. In particular, the IR spectrum of the decomposition products of **IVs** does not contain the characteristic skeleton vibration band of the *tert*-butoxy group at 875 cm^{-1}, and in the group of bands at 1400–1300 cm^{-1} belonging to symmetric bending modes of the Me_2C and Me_3C groups the band at 1365 cm^{-1} characteristic of the *tert*-butyl group [18] decreases in intensity. It should be noted that the IR spectra of decomposition products of peroxyalkynes **IVs**–**IVu** are virtually identical, suggesting similar mechanism of decomposition of these peroxides with formation of a similar set of nonvolatile decomposition products. In particular, in the IR spectra of the decomposition products, the bands at 725±5 and 1480±5 cm^{-1} characterizing vibrations of the $(CH_2)_x$ chain and bending vibrations of the methyl and methylene groups [18] are preserved; two bands of approximately equal intensity at 1385 and 1370 cm^{-1} suggest the presence of *gem*-dimethyl groups. There are also a number of characteristic bands absent in the IR spectra of the starting compounds **IVs**–**IVu**; strong bands at 1720 and 1680±5 cm^{-1} belong to carbonyl groups; a strong band at about 3400 cm^{-1} suggests the presence of a hydroxy group; bands of approximately equal intensity at 2240 and 2215±1 cm^{-1} are due to the presence of the C≡C bonds (in the spectra of the starting compounds **IVs**–**IVu**, there is a single C≡C stretching band at 2248±1 cm^{-1}) [18]. These data show that the products of thermal decompostion of **IVs**–**IVu** are complex mixtures of products of different structures, mainly hydroxy- and carbonyl-containing substances. These mixtures were separated into four major fractions by column chromatography (silica gel L 100/250 μm, Czechia; eluent hexane or hexane–diethyl ether). The ^{1}H NMR and IR spectra of these fractions revealed the presence of the following acetylenic compounds [18, 19]: 2-heneicosyne, 3-docosyn-2-one, 4-tricosyn-2-one, and 2-methoxy-3-docosyn-2-ol.

With the aim to assess the reliability of the characteristics of thermal stability of **I**–**VIII**, obtained by DTA, we calculated quantum-chemically the strength of the O–O bond in monosubstituted peroxyalkynes **Ia**–**Id**, long-chain peroxyalkynes **IVs**–**IVu**, and also 3-*tert*-alkyl-3-methylperoxy-1-butynes **Xa**–**Xc**, which are the starting compounds in the synthesis of disubstituted long-chain peroxyalkynes **IVa**–**IVu** and organosilicon diperoxides **VIIIa**–**VIIId**. For comparison, we also performed quantum-chemical calculations for peroxide **IX** and a disubstituted peroxyalkyne with

Table 2. Results of quantum-chemical calculations for peroxides **Ia–Id, IVs–IVu**, and **IX–XI**, alcohols ROH and R'OH, and radicals $RO^{\cdot}$ and $R'O^{\cdot}$

Comp. no.	H_f, kJ mol^{-1}	$\Delta H_{f,H}$, kJ mol^{-1}	$\Delta H_{f,R}$, kJ mol^{-1}	ROH, R'OH	$H_{f,ROH}$, $H_{f,R'OH}$, kJ mol^{-1}	$H_{f,RO^{\cdot}}$, $H_{f,R'O^{\cdot}}$, kJ mol^{-1}
Ia	25.255	–389.798	20.242	$MeCH_2Me_2COH$	–276.588	–38.685
Ib	93.052	–397.003	–	$Me(CH_2)_2MeCOH$	–294.734	–46.175
Ic	260.446	–383.305	–	$Me(CH_2)_4Me_2COH$	–351.623	–116.257
Id	604.998	–404.773	–	*cyclo*-$C_6H_{11}Me_2COH$	–291.031	–
IVs	–334.875	–377.911	–	$PhMe_2COH$	–109.939	–
IVt	–339.749	–380.953	–	Ph_3COH	213.146	–
IVu	–357.586	–381.263	–	$HC{\equiv}CMe_2COH$	–9.899	161.753
IX	168.745	–391.643	–	Me_3COH	–268.671	–30.547
Xa	97.914	–379.506	33.292	$Me(CH_2)_{17}C{\equiv}CMe_2COH$	–441.094	–
Xb	92.086	–381.593	30.983	H_2 [22]	3.021	
Xc	71.927	–379.581	43.652			
XI	–348.243	–386.903	–			

cycloalkylperoxy group, 2-methyl-2-(2-cyclohexyl-2-propylperoxy)-3-docosyne **XI**, which has not been described in the literature. Calculations were performed by the SCF MO LCAO semiempirical method in the MNDO valence approximation [1, 20, 21] with full optimization of the geometry. The calculated heats of formation (H_f) [20], hydrogenation, and cleavage of the O–O bond in the peroxides are listed in Table 2.

The MNDO calculations fairly adequately reproduce the structural characteristics of the compounds under consideration, except certain systematic underestimation of the O–O bond length by ~0.15 Å [1].

The heats of hydrogenation and cleavage of the O–O bond ($\Delta H_{f,H}$ and $\Delta H_{f,R}$) were calculated from the thermochemical equations

$$ROOR' + H_2 \longrightarrow ROH + R'OH,$$

$$\Delta H_{f,H} = (H_{f,ROH} + H_{f,R'OH} - [H_f + H_f(H_2)];$$

$$ROOR' \longrightarrow RO^{\cdot} + R'O^{\cdot},$$

$$\Delta H_{f,R} = (H_{f,RO^{\cdot}} + H_{f,R'O^{\cdot}}) - H_f.$$

The heat of formation of hydrogen, $H_f(H_2)$, is 3.021 kJ mol^{-1} [22].

The calculated heats of formation ($H_{f,ROH}$, $H_{f,R'OH}$, $H_{f,RO^{\cdot}}$, $H_{f,R'O^{\cdot}}$) of alcohols (ROH, R'OH) and radicals ($RO^{\cdot}$, $R'O^{\cdot}$) are listed in Table 2.

In optimization of the geometry of systems with open shells (radicals), it is necessary to use another approximation taking into account multielectron configuration interaction. This significantly alters the calculated energy characteristics of the systems and dramatically increases the time required for the calculation; therefore, we could not adequately calculate $\Delta H_{f,R}$ of decomposition of the peroxides into radicals and evaluated the strength of the O–O bonds in peroxyalkynes only by the calculated heats of hydrogenation $\Delta H_{f,H}$ (Table 2).

Table 2 shows that the results of quantum-chemical calculations are mainly consistent with the DTA data. As judged from the heats of hydrogenation, the O–O bond strength in mono- (**Ia**, **Xa**–**Xc**) and disubstituted (**IVs**–**IVu**) peroxyalkynes containing *tert*-alkylperoxy groups is somewhat higher compared to peroxyalkynes containing cycloalkyl- (**Ib**, **XI**) and aralkylperoxy (**Ic**, **Id**) groups (the heats of hydrogenation of **Ia**, **IVs**–**IVu**, and **Xa**–**Xc** are lower than those of **Ib**–**Id** and **XI** by ~13 kJ mol^{-1} on the average). In the series of alkyl peroxides **Ia**, **IVs**–**IVu**, and **Xa**–**Xc**, in conformity with the conclusions made from the thermal decomposition data, the strength of the O–O bond (heat of hydrogenation) decreases in going from compounds with the *tert*-butylperoxy group (**IVs**, **Xa**) to those with *tert*-pentylperoxy (**IVt**, **Xb**), 2-methyl-2-pentylperoxy (**IVu**, **Xc**), and 2-methyl-2-heptylperoxy (**Ia**) groups. Certain inconsistency between the data on thermal stability of peroxide **IX** and aralkyl peroxide **Ic**, on the one hand, and on the heats of their hydrogenation (quantum-chemical calculations), on the other hand, may be due to the fact that, in going from peroxide **IX** to aralkyl peroxide **Ic**, the thermal decomposition pattern appreciably changes, which may be associated with increased contribution of induced decomposition in the case of **Ic**. Somewhat higher O–O bond strength in **X** relative to the starting peroxyalkyne **Ib** (Table 2) is also consistent with the enhanced thermal stability of disubstituted peroxyalkynes compared to monosubstituted peroxyalkynes (Table 1).

EXPERIMENTAL

The IR spectra were taken on a Specord IR-75 spectrophotometer (thin films). The ^1H NMR spectra were recorded on a Tesla BS-567A spectrometer ($CDCl_3$, internal reference tetramethylsilane).

Peroxides **I**–**VIII** were prepared and purified for derivatographic experiments according to [3–10].

Thermolysis of peroxides was performed on a Paulik–Paullik–Erdey derivatograph at a linear heating rate of 7 deg min^{-1} (for **Id**, 5.7; for **IX**, 10 deg min^{-1}). The sample weight was 100 mg. As inert material we used Al_2O_3 (100 mg) calcined to 1200°C. For complete removal of air from the crucible, the reaction volume was purged with argon. The argon supply was started 1 h before the beginning of heating and was continued throughout the experiment. The sensitivity parameters were as follows: balance 100 mg, DTA 1/10, and DTG 1/10. The reaction order (*n*) of thermal decomposition of peroxides **I**–**VIII** was calculated from the DTA curves by the Kissinger method [2]. The activation energy was calculated from the DTA curves [12] with the equation $\ln\Delta T = \mathrm{const} - E/RT$, where ΔT is the temperature difference between the inert reference and sample being analyzed, corresponding to the height of the exo peak from the baseline at a given temperature within the range of the substance thermolysis). Since ΔT is proportional to the peak height, the height of the exo peak was expressed in millimeters. ΔT was measured in 2.5°C steps along the temperature line. E_a was determined from the slope of the straight line $\ln\Delta T$–$10^3/T$ in the portion in which this dependence is linear.

For monoperoxyalkynes **Ia**, **Ic**, and **Id**, diperoxides **Va**–**Vc**, **VIa**, and **VIIIa**–**VIIIc**, and peroxide **IX**, the dependence $\ln\Delta T$–$10^3/T$ remains linear up to ~150°C; for monoperoxyalkynes with cyclohexylperoxy group (**Ib**, **Ie**) and diacetylenic diperoxides **VIIa**–**VIIc**, up to ~140°C; for disubstituted peroxyalkynes with trimethylsilyl groups (**IIb**, **IIc**, **Ve**) and peroxyalkynes **IVa**–**IVu**, up to ~160–170°C; and for peroxyalkynes with triphenylsilylperoxy groups (**IIIa**–**IIIf**), up to ~175–180°C.

The quantum-chemical calculations were performed by the GAMESS program [23].

To study nonvolatile decomposition products of peroxyalkynes **IVs**–**IVu**, 200-mg samples of the substances were heated to 200°C (end of the first decomposition step) under the conditions of derivatographic measurements, after which the crucible with the nonvolatile residue was removed from the chamber and cooled. The reaction products were dissolved in diethyl ether and analyzed after removing the solvent and drying in a vacuum (TLC on Silufol UV-254 plates; ^1H NMR and IR spectroscopy).

Separation of mixtures of reaction products was performed by column chromatography on silica gel L 100/250 μm (Czechia). Initially we used hexane as eluent and isolated a fraction consisting predominantly of 2-heneicosyne. IR spectrum, ν, cm^{-1}: 2970, 2340, 2870 [$\nu(CH_3)$, $\nu(CH_2)$], 1470 [$\delta_{as}(CH_2)$, $\delta_{as}(CH_3)$], 1380 [$\delta_s(CH_3)$], 725 {$\delta[(CH_2)_x]$}. ^1H NMR spectrum, δ, ppm: 0.78 t (CH_3CH_2), 1.20–1.40 m [$(CH_2)_x$], 1.70–2.00 m ($CH_3C\equiv C$, $C\equiv CCH_2$). With hexane–diethyl ether, 100 : 1, as eluent, we isolated a fraction containing an appreciable amount of an α-acetylenic ketone, 3-docosyn-2-one. IR spectrum, ν, cm^{-1}: 1685 (C=O), 2215 ($C\equiv C$). ^1H NMR spectrum, δ, ppm: 0.88 t (CH_3CH_2), 1.10–1.38 m [$(CH_2)_x$], 2.17 t ($CH_2C\equiv C$), 2.33 s [$CH_3C(O)$]. With hexane–diethyl ether, 100 : 5, as eluent, we obtained a fraction consisting mainly of an acetylenic alcohol, 2-methyl-3-docosyn-2-ol. IR spectrum, ν, cm^{-1}: 3610–3125, 1340, 1150 (OH), 1385, 1365, 1170, 860 [$(CH_3)_2C$], 2245 ($C\equiv C$). ^1H NMR spectrum, δ, ppm: 0.88 t (CH_3CH_2), 1.10–1.43 m [$(CH_2)_x$], 1.48 s [$(CH_3)_2C$], 1.83 br.s (OH), 2.17 t ($CH_2C\equiv C$). With hexane–diethyl ether, 100 : 10 and 100 : 25, as eluent, we obtained two identical fractions containing a mixture of an alcohol, 2-methyl-3-docosyn-2-ol, and an acetylenic ketone with the carbonyl group remote from the triple bond, 4-tricosyn-2-one. IR spectrum, ν, cm^{-1}: 1735 (C=O). ^1H NMR spectrum, δ, ppm: 0.87 t (CH_3CH_2), 1.12–1.45 m [$(CH_2)_x$], 2.08–2.30 m [$CH_2C\equiv C$, $H_3C(O)$].

REFERENCES

1. Yuvchenko, A.P., Dikusar, E.A., Kozlov, N.G., Zelenkovskii, V.M., Prokopchuk, N.R., Filanchuk, L.P., and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 1, p. 111.
2. Wendlandt, W.Wm., *Thermal Methods of Analysis*, New York: Interscience, 1964.
3. Yuvchenko, A.P., Moiseichuk K.L., Dikusar, E.A., and Ol'dekop, Yu.A., *Vestsi Akad. Navuk Bel. SSR, Ser. Khim. Navuk*, 1995, no. 2, p. 65.
4. Yuvchenko, A.P., Dikusar, E.A., Zhukovskaya, N.A., and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 1992, vol. 62, no. 11, p. 2604.
5. Yuvchenko, A.P., Dikusar, E.A., Zhukovskaya, N.A.,

and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 1993, vol. 63, no. 1, p. 143.

6. Dikusar, E.A., Yuvchenko, A.P., Zhukovskaya, N.A., and Moiseichuk, K.L., *Zh. Org. Khim.*, 2000, vol. 36, no. 2, p. 195.
7. Milas, N.A. and Mageli, O.L., *J. Am. Shem. Soc.*, 1952, vol. 74, no. 6, p. 1471.
8. Yuvchenko, A.P., Moiseichuk, K.L., Dikusar, E.A., Zhukovskaya, N.A., and Ol'dekop, Yu.A., *Zh. Obshch. Khim.*, 1990, vol. 60, no. 7, p. 1587.
9. Yuvchenko, A.P., Moiseichuk, K.L., Dikusar, E.A., and Ol'dekop, Yu.A., *Zh. Org. Khim.*, 1984, vol. 20, no. 12, p. 2526.
10. Yuvchenko, A.P., Moiseichuk, K.L., and Dikusar, E.A., *Zh. Org. Khim.*, 1989, vol. 25, no. 6, p. 1160.
11. Prokopchuk, N.R., *Vestsi Akad. Navuk Bel. SSR, Ser. Khim. Navuk*, 1984, no. 4, p. 119.
12. Gorshkov, V.S., Timashev, V.V., and Savel'ev, V.G., *Metody fiziko-khimicheskogo analiza vyazhushchikh veshchestv* (Methods of Physicochemical Analysis of Binders), Moscow: Vysshaya Shkola, 1981, p. 37.
13. *Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 1.
14. Rakhimov, A.I., *Khimiya i tekhnologiya organicheskikh perekisnykh soedinenii* (Chemistry and Technology of Organic Peroxy Compounds), Moscow: Khimiya, 1979, p. 63.
15. Dikusar, E.A., Yuvchenko, A.P., Zelenkovskii, V.M., Zhukovskaya, N.A., and Moiseichuk, K.L., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 6, p. 984.
16. Denisov, E.T., *Konstanty skorosti gomoliticheskikh zhidkofaznykh reaktsii* (Rate Constants of Homolytic Liquid-Phase Reactions), Moscow: Nauka, 1971.
17. Broido, A. and Semple, A., *J. Polym. Sci., Part A-2*, 1969, vol. 7, no. 10, p. 1761.
18. Bellamy, L.J., *The Infra-Red Spectra of Complex Molecules*, New York: Wiley, 1957.
19. Ionin, B.I., Ershov, B.A., and Kol'tsov, A.I., *YaMR-Spektroskopiya v organicheskoi khimii* (NMR Spectroscopy in Organic Chemistry), Leningrad: Khimiya, 1983.
20. Dewar, M.J.S. and Thiel, W., *J. Am. Chem. Soc.*, 1977, vol. 99, no. 15, p. 4899.
21. Baker, J., *J. Comput. Chem.*, 1986, vol. 7, no. 4, p. 385.
22. Stewart, J.J.P., *J. Comput. Chem.*, 1989, vol. 10, no. 4, p. 221.
23. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S.J., Mindus, T.L., Dupnis, M., and Montgomery, J.A., *J. Comput. Chem.*, 1993, vol. 14, no. 7, p. 1347.