Experimental and quantum-chemical investigation of thermolysis of adamantyl-substituted organosilicon peroxides

B. I. Nho,[a] G. M. Butov,[a] S. Yu. Dumskii,[a] Z. M. Sabirov,[b] V. N. Urazbaev,[b] and Yu. B. Monakov[b]*

[a]*Volgograd State Technical University,*
28 prosp. Lenina, 400066 Volgograd, Russian Federation.
Fax: +7 (844 2) 34 4121. E-mail: tons@.vstu.tsaritzyn.su
[b]*Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences,*
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 5107. E-mail: root@.chemorg.bashkiria.su

The kinetics and mechanism of thermal decomposition of adamantyl-containing organosilicon peroxides in a solution in *n*-nonane were studied. The relationship between the structure of the peroxide and the rate and mechanism of thermolysis was established. The effect of the peroxide structure on the electronic characteristics of the peroxide bond was studied by the MNDO method. The heterolytic rearrangement occurring during the decomposition of peroxides was analyzed.

Key words: adamantane, organosilicon peroxides; thermolysis; MNDO.

Development of new polymeric materials calls for broadening and renewal of the existing set of radical initiators, especially those for high-temperature homolytic processes. Organosilicon peroxides containing an adamant-1-yl group[1—2] are promising initiators for high-temperature processes. Previously,[3] efficient methods for the synthesis of these compounds have been developed; however, there are no data on the kinetics and mechanism of their thermal transformations and on the effect of the adamantyl radical on the stability of the peroxide bond. In this work, we studied the kinetics of thermal decomposition of adamantyl-containing organosilicon peroxides Ad—X—$SiMe_2OOCMe_3$ (**1a—g**). For comparison, we also studied peroxides R—$SiMe_2OOCMe_3$ (**2a—c**), which have a similar structure but contain no adamantyl radical.

Ad—X—$SiMe_2OOCMe_3$
1a—g

X = CH_2CH_2 (**a**), *p*-$C_6H_4CH_2$ (**b**), O (**c**), CH_2O (**d**), CH_2CH_2O (**e**), *p*-C_6H_4 (**f**), *p*-$C_6H_4CH_2CH_2$ (**g**)

R—$SiMe_2OOCMe_3$
2a—c

R = Et (**a**),[1] $PhCH_2$ (**b**),[2] Me_3CO (**c**)[3]

Experimental

Kinetic studies were carried out by the ampule method.[4] The contents of peroxides were determined by iodometry.[4] The composition of the mixture of the thermolysis products was studied by GLC. Gaseous products of decomposition of peroxides were determined by GC using a KhL-4 chromatograph (HTD, a 2-m long steel column, 15% of GEGNMK on Spherochrom, H_2 as the carrier gas, detector temperature 45 to 50 °C, and air as the standard). Liquid products of decomposition were analyzed on a Tsvet-104 chromatograph (HTD, a 2-m long steel column, Carbowax 20M (15%) on Chromaton N-AW, nitrogen as the carrier gas, column temperature 50 °C).

The products of rearrangement were isolated by vacuum distillation. Their composition and structure were confirmed by known methods of analysis, ^1H NMR and IR spectroscopy, and by an alternative synthesis.

The IR spectra of the compounds synthesized were recorded on UR-20 and Specord M-82 spectrophotometers. Liquids were studied as thin films, while solids were analyzed in vaseline oil. The basicity of peroxides was studied on a UR-20 spectrophotometer in the 3300—3700 cm^{-1} range by a known procedure.[5] To measure the $\Delta\nu$ values, the peroxide under study was added to a solution of phenol in CCl_4 (0.02 mol L^{-1}). The concentration of the peroxide in the solution was 0.25—0.3 mol L^{-1}. The second channel of the spectrophotometer contained a reference cell filled with a CCl_4 solution of the peroxide. The absorbing layer of the solutions was 1.01 mm thick.

The ^1H NMR spectra of compounds were recorded on Tesla BS 487 (100 MHz) and Bruker AC-200P (300 MHz) spectrometers in CCl_4 or $CDCl_3$ using HMDS or $CHCl_3$ as the internal standards.

Synthesis of organosilicon peroxides 1a—e (general procedure). Peroxides **1a—e** were prepared from the corresponding adamantyl-containing organochlorosilanes[6,7] and *tert*-butyl hydroperoxide (TBH). (Adamant-1-yloxy)chlorodimethylsilane (0.022 mol, 5.48 g) and diethyl ether (50 mL) were placed in a four-necked flask equipped with a stirrer, a thermometer, a bubbler, and a condenser. The solution was cooled with stirring to −10 °C, then an ethereal solution of TBH (0.024 mol, 2.12 g) was added, and the mixture was cooled to 0 °C. Then ammonia, dried over KOH, was fed at such a velocity as to maintain the temperature in the reactor below 20 °C. The reaction time was 20—30 min. After that, the reaction mixture was stirred for 60 min, and filtered from the precipitated ammonium chloride.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1317—1320, July, 1998.

Table 1. Kinetic and activation parameters of decomposition of peroxides **1** and **2** in *n*-nonane (the overall process) (C_0 = 0.05 mol L^{-1})

Per-	$k \cdot 10^5$/s^{-1} at T/K						E_a	log$A$	$\Delta S^{\neq}$
oxide	433	443	453	463	473	483	/kJ mol^{-1}		/J mol^{-1} deg^{-1}
1a			2.38	6.30	14.02	34.71	163.45	14.23	3.68
1b	6.49	12.36	28.30	61.78			123.76	10.73	−12.24
1c			3.02	6.04	14.85	27.85	138.69	11.34	−39.90
1d			4.18	10.31	20.13	35.55	139.63	11.72	−32.68
1e			4.96	9.49	22.72	50.16	143.23	12.03	−26.71
2a			2.16	5.26	12.18	27.42	154.36	13.10	−1.48
2b	4.45	9.26	23.80	45.94			133.72	11.75	−7.55
2c			2.63	4.71	9.96	21.06	128.18	9.66	−72.10

The filtrate was concentrated to remove the diethyl ether. The residue was evacuated for 1 h at 50—60 °C to remove excess TBH. Peroxide **1c** was purified by vacuum distillation (b.p. 170 °C/0.5 Torr) or by column chromatography on the KSK-2 silica gel using *n*-hexane as the eluent.

[2-(Adamant-1-yl)ethyl]dimethyl(*tert*-butylperoxy)silane (1a), yield 69%; n_D^{20} 1.4849, d_4^{20} 0.9945, R_f 0.82 (ether—hexane, 2 : 1). Found (%): C, 70.05; H, 11.76; Si, 9.05; O_{act}, 5.06. MR_D, 89.46. $C_{18}H_{34}SiO_2$. Calculated (%): C, 69.61; H, 11.03; Si, 9.04; O_{act}, 5.13. MR_D, 89.95. IR, ν/cm^{-1}: 783 (Si—O); 850 (C—O—O—); 905 (O—O). ^{1}H NMR, δ: 0.23 (t, 3 H, CH_2Si); 1.02 (s, 9 H, CMe_3); 1.31, 1.50, 1.82 (all s, 15 H, $C_{10}H_{15}$).

(*para*-Adamant-1-ylbensyl)dimethyl(*tert*-butylperoxy)silane (1b), yield 74%, m.p. 90 °C (from hexane), R_f 0.80 (ether—hexane, 2 : 1). Found (%): C, 73.86; H, 9.44; Si, 7.30; O_{act}, 4.26. $C_{23}H_{36}SiO_2$. Calculated (%): C, 74.13; H, 9.73; Si, 7.54; O_{act}, 4.28. IR, ν/cm^{-1}: 850 (C—O—O—); 900 (O—O). ^{1}H NMR, δ: 1.05 (s, 9 H, CMe_3); 1.65, 1.77, 1.95 (all s, 15 H, $C_{10}H_{15}$); 2.05 (s, 2 H, CH_2); 6.76, 6.99 (both d, 4 H, C_6H_4, J_O = 8 Hz).

(Adamant-1-yloxy)dimethyl(*tert*-butylperoxy)silane (1c), yield 97%; n_D^{20} 1.4696, d_4^{20} 1.0256. Found (%): C, 64.08; H, 10.40; Si, 8.90; O_{act}, 5.28. $C_{16}H_{30}SiO_3$. Calculated (%): C, 63.92; H, 10.77; Si, 9.34; O_{act}, 5.32. IR, ν/cm^{-1}: 850 (C—O—O—); 900 (O—O). ^{1}H NMR, δ: 0.16 (s, 6 H, 2 Me); 1.206 (s, 9 H, CMe_3); 1.56, 1.79, 2.07 (all s, 15 H, $C_{10}H_{15}$).

(Adamant-1-ylmethoxy)dimethyl(*tert*-butylperoxy)silane (1d), yield 95%; n_D^{20} 1.4698, d_4^{20} 1.0045. Found (%): C, 65.80; H, 10.53; Si, 9.03; O_{act}, 5.08. $C_{17}H_{32}O_3Si$. Calculated (%): C, 64.86; H, 10.97; Si, 8.92; O_{act}, 5.08. IR, ν/cm^{-1}: 850 (C—O—O—); 900 (O—O).

[2-(Adamant-1-yl)ethoxy]dimethyl(*tert*-butylperoxy)silane (1e), yield 74%; n_D^{20} 1.4701, d_4^{20} 1.0038. Found (%): C, 66.16; H, 10.67; Si, 8.02; O_{act}, 4.85. Found (%): C, 66.16; H, 10.97; Si, 8.33; O_{act}, 4.85. $C_{18}H_{34}O_3Si$. Calculated (%): C, 65.72; H, 11.15; Si, 8.54; O_{act}, 4.86. IR, ν/cm^{-1}: 850 (C—O—O—); 900 (O—O).

Results and Discussion

Thermal decomposition of peroxides **1** and **2** in a solution in *n*-nonane was studied in the 413—483 K temperature range. Since decomposition of organosilicon peroxides **1** is sensitive to the polarity of the medium,[8] we chose *n*-nonane as the solvent, because it is largely inert in complexation reactions involving silicon compounds.[9]

The process of decomposition of peroxides **1** is described by a first-order kinetic equation up to a degree of conversion of 70—90%. The temperature dependence of the decomposition rate constants obeys the Arrhenius equation.

The kinetic and activation parameters were calculated by the least-squares method according to the IUPAC recommendations.[10]

A tenfold change in the initial peroxide concentration (0.01—0.1 mol L^{-1}) has no effect on the rate constant, indicating that no step of induced decomposition is involved.

The reaction rate constants and activation parameters are presented in Table 1.

To elucidate the influence of the adamantyl substituent on the kinetics and mechanism of thermolysis, we analyzed the products formed upon the decomposition of peroxides (Table 2).

The formation of acetone, methane, and *tert*-butyl alcohol points to the radical cleavage of the peroxide bond.

$$\mathrm{Ad{-}X{-}SiMe_2OOCMe_3} \xrightarrow{k_1} \mathrm{Ad{-}X{-}SiMe_2O^{\cdot}} + {}^{\cdot}\mathrm{OCMe_3}$$

$$^{\cdot}\mathrm{OCMe_3} \longrightarrow {}^{\cdot}\mathrm{CH_3} + \mathrm{Me_2CO}$$

$$^{\cdot}\mathrm{OCMe_3} + \text{solvent} \longrightarrow \mathrm{HOCMe_3}$$

$$^{\cdot}\mathrm{CH_3} + \text{solvent} \longrightarrow \mathrm{CH_4}$$

However, along with the homolytic decomposition of the peroxide, heterolytic rearrangement yielding products **3** and **4** also takes place.

Table 2. Yields of the products of thermolysis of peroxides **1** and **2** in *n*-nonane (453 K, C_0 = 0.1 mol L^{-1})

Per-	Yield of the product[a] (%)			
oxide	CH_4	Me_2CO	Bu^{t}OH	RP[b]
1a	0.39	0.40	0.60	—
1b	0.095	0.104	0.085	0.80
2a	0.24	0.22	0.51	0.25
2b	0.08	0.075	0.064	0.86

[a] Mole per mole of the peroxide. [b] RP is rearrangement product **3** or **4**.

Table 3. Rate constants for homolytic (k_1) and heterolytic (k_2) decomposition of peroxides **1** and **2** (180 °C, *n*-nonane)

Per- oxide	$k \cdot 10^5$	$k_1 \cdot 10^5$ s^{-1}	$k_2 \cdot 10^5$
1a	2.38	2.38	—
1b	28.30	3.96	24.30
1c	3.02	3.02	—
1d	4.18	4.18	—
1e	4.96	4.96	—
1f	18.60	1.40	17.20
1g	8.17	2.63	5.54
2a	2.16	1.62	0.54
2b	23.80	3.96	19.84
2c	2.63	2.63	—

$$\underset{\mathbf{1}}{\text{Ad—X—SiMe}_2\text{OOCMe}_3} \xrightarrow{k_2} \underset{\mathbf{3}}{\text{Ad—X—OSiMe}_2\text{OCMe}_3}$$

$$\underset{\mathbf{2}}{\text{R—SiMe}_2\text{OOCMe}_3} \xrightarrow{k_2} \underset{\mathbf{4}}{\text{R—OSiMe}_2\text{OCMe}_3}$$

The proportion of the peroxide decomposing according to the rearrangement pattern depends on the nature of the migrating AdX and R groups; in terms of their influence, these groups can be arranged in the following sequence:

$AdC_6H_4CH_2 \equiv C_6H_4CH_2 > AdC_6H_4 > AdC_6H_4C_2H_4 \equiv Et \equiv AdC_2H_4$.

Peroxide **1a** virtually does not rearrange, as indicated by the quantitative yield of the products of radical decomposition and also by the absence of **3a** (X = CH_2CH_2).

Based on the ratio of the radical decomposition products to products **3** and **4** and assuming that the rate constant for the overall process (k) is the sum of the rate constants for the homolytic (k_1) and heterolytic (k_2) reaction routes, we calculated the rate constants for both routes of transformation of peroxides **1** and **2** (Table 3).

Comparison of the rate constants k_1 demonstrates that the structure of the substituent at the Si atom has only a slight effect on the rate of homolytic decomposition.

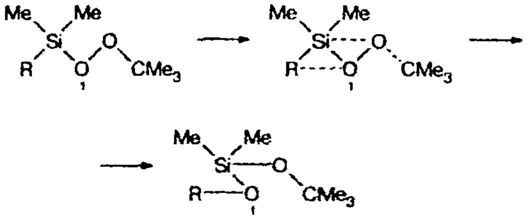
The heterolytic rearrangement is more sensitive to variation of the AdX and R substituents at the Si atom in the peroxides. Heterolysis does not occur when these are alkoxy groups; it occurs to a small extent (up to 25%) in the case of alkyl substituents, and predominates (up to 85%) in the case of peroxides whose substituents contain benzene rings. Attention is attracted by the character of variation of k_2 on going from compound **1f** to **1a**, and then to **1g** (see Table 3). When the distance between AdC_6H_4 and the Si atom increases (on going from **1f** to **1a**), the constant k_2 increases, but on further separation (on going from **1a** to **1g**), this constant sharply decreases.

To interpret the results obtained, we carried out MNDO calculations of the geometric and electronic structures of organosilicon peroxides.[11] The calculations showed that variation of the nature of the AdX and R substituents in the peroxides $AdXSiMe_2OOCMe_3$ (**I**) and $RSiMe_2OOCMe_3$ (**2**) influences only slightly the electronic structure of the peroxide bond. In fact, the charges on the O atoms change by no more than 0.05 (e), and the O—O bond order changes by 0.01.

This is consistent with the experimental data (see Table 1), indicating that the structure of the AdX and R substituents in compounds **1** and **2** has a weak effect on the rate of homolytic decomposition.

To rationalize the change in the k_2 value in the series **1f** → **1a** → **1g** (see Table 3), we carried out quantum-chemical calculations of the structures of peroxides **1f**, **1a**, and **1g** in the initial, transition, and final states of the heterolytic rearrangement. According to the published data,[12] the rearrangement occurs *via* a four-membered cyclic transition complex (Scheme 1).

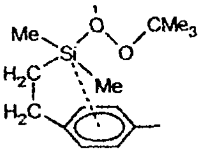
Scheme 1



The transition states were investigated by MNDO calculations using the SADDLE procedure (search for the saddle point[13]) included in the MOPAC program package (Table 4).

It can be seen from the data given in Table 4 that the height of the barrier (*i.e.*, the energy needed to reach the transition state) for $AdC_6H_4SiMe_2OOCMe_3$ (**1f**) amounts to 144 kJ mol^{-1}. On going to the compound $AdC_6H_4CH_2SiMe_2OOCMe_3$ (**1a**), the barrier somewhat decreases and becomes equal to 135 kJ mol^{-1}. Therefore, the k_2 value for compound **1a** is somewhat greater than that for **1f**. However, the compound $AdC_6H_4CH_2CH_2SiMe_2OOCMe_3$ (**1g**) in the initial state tends to form an intramolecular complex with a complexation energy of 23 kJ mol^{-1} in which the Si atom is bound to the π-orbitals of the C atoms of the benzene ring (Scheme 2).

Scheme 2



The total order of the bond of Si with the aromatic-ring C atoms amounts to 0.15. Hence, the barrier to the heterolytic rearrangement of compound **1g** increases by the magnitude of the complexation energy and is equal to 167 kJ mol^{-1}. Consequently, the k_2 value appreciably decreases.

Comparison of the k_2 constants for peroxides **1b** and **2b** (see Table 3) indicates that upon introduction of an adamantyl radical into the *para*-position of the aryl-

Table 4. Total energy (*E*), bond lengths (*d*/Å), and bond orders (*W*) in the initial, transition, and final states of the molecule $AdC_6H_4SiMe_2OOCMe_3$ in the heterolytic rearrangement

State	*E*	Si—C*		Si—O(1)		Si—O(2)		O(1)—O(2)		O(1)—C	
	/kJ mol^{-1}	*d*	*W*	*d*	*W*	*d*	*W*	*d*	*W*	*d*	*W*
Initial	0	1.83	0.83	1.71	0.75	2.53	0.01	1.28	0.98	2.74	0.01
Transition	144	2.24	0.22	1.73	0.73	1.81	0.57	1.90	0.31	1.54	0.75
Final	−92	2.84	0.02	1.71	0.75	1.71	0.73	2.62	0.01	1.34	1.02

Note. The energy of the initial state was taken to be zero. * The carbon atom of the benzene ring.

containing substituent, the rate constant for heterolysis increases to an even greater extent, which is apparently due to the increase in the nucleophilicity of the migrating group. In order to confirm this hypothesis, the basicity of peroxides **1b** and **2b** was studied by IR spectroscopy.[5] This was done by investigating the formation of a hydrogen bond between the peroxide and phenol. It was assumed that the higher the electron density on the peroxide O atoms, the greater the shift of the O—H stretching frequency ($\Delta\nu$/cm^{-1}) in non-associated phenol:

Peroxide	$\Delta\nu'$(O—O)	$\Delta\nu''$(C_6H_4)
1b	193	85
2b	190	60

Here $\Delta\nu'$ is the difference between the OH stretching frequencies in non-associated phenol and in the —OH...O—O— complex; $\Delta\nu''$ is the difference between the OH stretching frequencies in non-associated phenol and in the —OH...π-C_6H_4 complex.

The frequency change $\Delta\nu''$(C_6H_4) associated with the second type of association is relatively large (20—25 cm^{-1}), indicating that the electron density on the aromatic ring somewhat increases and, therefore, the nucleophilicity of *p*-adamant-1-ylbenzyl radical is enhanced. In addition, the ^{1}H NMR signals of the protons of the methylene group in peroxide **1b** (2.05 ppm) are shifted upfield in relation to the corresponding signals in the spectrum of peroxide **2b** (2.09 ppm); this points to an increase in the electron density on these protons.

Peroxide **1a** mostly decomposes by the homolytic route, which is confirmed by the composition of the thermolysis products, by the high activation energy of this reaction, and by its positive activation entropy (see Table 1). Evidently, the steric influence of the adamantyl group hampers the formation of the cyclic transition complex (see Scheme 2) and, hence, suppresses the heterolysis.

Thus, the structure of substituents AdX and R in peroxides Ad—X—$SiMe_2OOCMe_3$ and R—$SiMe_2OOCMe_3$ exert only a slight effect on their homolytic decomposition. Heterolytic rearrangement is more sensitive to the variation of substituents AdX and R at the Si atom. The formation of intramolecular complexes in the compounds under study can have a substantial influence on the ratio of homolytic and heterolytic routes of decomposition of adamantyl-containing organosilicon peroxides.

References

1. N. P. Sluchevskaya, N. V. Yablokova, V. A. Yablokov, and Yu. A. Aleksandrov, *Zh. Obshch. Khim.*, 1978, **48**, 1136 [*J. Gen. Chem. USSR*, 1978, **48** (Engl. Transl.)].
2. B. I. Nho, G. M. Butov, and A. D. Kim, *Khimiya i prakticheskoe primenenie kremnii- i fosfororganicheskikh soedinenii* [*Chemistry and Applications of Organosilicon and Organophosphorus Compounds*], LTI, Leningrad, 1980, 127 (in Russian).
3. Yu. A. Aleksandrov, N. V. Yablokova, and V. A. Yablokov, *Khimiya elementoorganicheskikh soedinenii* [*Chemistry of Heteroorganic Compounds*], Izd-vo Gor'kovskogo Gos. Univ, Gor'kii, 1979, 7, 3 (in Russian).
4. A. D. Kim, N. V. Golubchenko, and G. M. Butov, in *Khimiya i tekhnologiya elementoorganicheskikh poluproduktov i polimerov* [*Chemistry and Technology of Heteroorganic Polymers and Intermediates*], VPI, Volgograd, 1984, 164 (in Russian).
5. S. E. Skobeleva, N. S. Vyazankin, S. Ya. Khorshev, A. N. Egorochkin, V. A. Yablokov, A. P. Tarabarina, A. N. Sunin, and N. V. Yablokova, *Zh. Obshch. Khim.*, 1973, **43**, 1514 [*J. Gen. Chem. USSR*, 1973, **43** (Engl. Transl.)].
6. G. M. Butov, A. D. Kim, and S. V. Bondarenko, *Khimiya elementoorganicheskikh soedinenii* [*Chemistry of Heteroorganic Compounds*], Izd-vo Gor'kovskogo Gos. Univ., Gor'kii, 1986, 24.
7. K. R. Saad, Ph. D. (Chem.) Thesis, Volgograd, 1996, 134 (in Russian).
8. V. A. Yablokov, N. V. Yablokova, A. P. Tarabarina, and M. N. Shemuranova, *Zh. Obshch. Khim.*, 1971, **41**, 1565 [*J. Gen. Chem. USSR*, 1971, **41** (Engl. Transl.)].
9. A. P. Tarabarina, Ph. D. (Chem.) Thesis, Izd-vo Gor'kovskogo Gos. Univ, Gor'kii, 1972 (in Russian).
10. *Rekomendatsii po predstavleniyu rezul'tatov khimicheskogo analiza* [*Recommentations on the Presentation of Results of Chemical Analysis*], *Zh. Anal. Khim.*, 1972, **26**, 1021 [*Russ. J. Anal. Chem.*, 1972, **26** (Engl. Transl.)].
11. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.
12. V. A. Yablokov, *Usp. Khim.*, 1980, **49**, 1711 [*Russ. Chem. Rev.*, 1980, **49** (Engl. Transl.)].
13. M. J. S. Dewar, E. F. Healy, and J. P. Stewart, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 227.

Received May 22, 1997;
in revised form December 5, 1997