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REACTIONS OF ORGANOELEMENT PEROXIDES OF THE SILICON SUBGROUP WITH OLEFINS

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Summary

The kinetic and activation parameters of decomposition of silicon subgroup organoelement peroxides R_3EOOR' (where E = Si, Ge, Sn; R = Me, Et; R' = CMe_3, CMe_2Ph) in olefins have been determined.

It is shown by the kinetic and thermochemical method that R_3EOOR' and olefins form complexes having 1 : 1 composition. For comparison, the complexing ability of the peroxide with pyridine, triethylamine and chloroform was evaluated. The stability constants (C_s) and the enthalpies of formation (ΔH) of the complexes were estimated from enthalpy values of mixing $Et_3SnOOCMe_3$ with ligands at 298.15 K. The formation of the peroxide—ligand complex is shown to depend upon both the nature of the peroxide and the ligand basicity. The competitive reactions of organoelement oxyradicals $R_3EO\cdot$ in olefins have been studied. The nature of the heteroelement, olefin and the reaction temperature have an influence upon the competitive ability of $R_3EO\cdot$ to add the olefin multiple bond or react via hydrogen abstraction. The probability of the addition reaction decreases in the series: $R_3SiO\cdot > R_3GeO\cdot > R_3CO\cdot$. The rate of reaction of hydrogen abstraction from the olefin molecule increases in the same series.

Introduction

The thermal decomposition of organoelement peroxides of the silicon subgroup has been studied only in saturated and aromatic hydrocarbons [1—3]. The primary reactions in these solvents are a spontaneous decay of peroxide with homolytical scission of the peroxide bond, rearrangement of initial peroxide into a nonperoxide product and interaction of peroxide with solvent (SH) (eq. 1—3).

$$R_3EOOR' \rightarrow R_3EO\cdot + R'O\cdot \qquad (1)$$

$$R_3EOOR' \rightarrow R_2(RO)EOR' \qquad (2)$$

TABLE 1

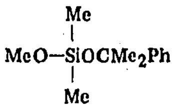
KINETIC AND ACTIVATION PARAMETERS OF PEROXIDE DECOMPOSITION IN OLEFINES (C_0 = 0.2 mol l^{-1}) [a]

Olefine	Peroxide														
	$Me_3SiOOCMe_3$			$Me_3SiOOCPhMe_2$			$Et_3GeOOCMe_3$			$Et_3SnOOCMe_3$			$Et_3SnOOCMe_2Ph$		
	k_{190} × 10^5 (sec^{-1})	E (kcal mol^{-1})	lg k_0	k_{190} × 10^5 (sec^{-1})	E (kcal mol^{-1})	lg k_0	k_{190} × 10^5 (sec^{-1})	E (kcal mol^{-1})	lg k_0	k_{150} × 10^5 (sec^{-1})	E (kcal mol^{-1})	lg k_0	k_{150} × 10^5 (sec^{-1})	E (kcal mol^{-1})	lg k_0
n-Nonane [b]	5.1	41.1	14.5	6.6	41.9	14.6	5.5	35.0	12.3	2.7	34.3	13.7	9.2	32.1	12.7
1-Heptene	4.5	38.8	14.0	6.7	40.3	14.8				5.3	24.8	8.5	17.8		
Styrene	5.9	40.2	14.8	8.6	39.6	14.7				61.4	28.6	11.5			
α-Methylstyrene	6.2	36.6	13.1	8.3	39.4	14.5	4.7	39.4	14.3	11.1	23.9	8.4	46.0	26.5	10.2
Tri-isobutylene	7.0	27.9	9.0	9.5	32.7	11.4									
Cyclohexene	8.4	31.7	11.0	13.3	34.7	12.5	13.4	28.6	9.6	13.7	22.4	7.7	46.9	23.6	8.8
1,1-Diphenylethylene	14.1	29.1	9.9	15.3	34.0	12.1	11.5	26.7	8.7	56.2	20.5	7.3	95.0		
Anethole	14.5	29.1	9.8	18.0	36.1	13.3									

[a] E and lg k_0 values are calculated by the least squares method, the mean square errors would not exceed ±1.4 kcal mol^{-1} and ±0.5, respectively. [b] These data are given for comparison.

TABLE 2

THE MAIN DECOMPOSITION PRODUCTS OF $Me_3SiOOCMe_2Ph$ IN OLEFINS (IN MOLES PER MOLE OF PEROXIDE) (C_0 = 0.2 mol l^{-1}, T = 200°C)

Solvent	Me_3SiOH	 $PhC(=O)Me$	$PhMe_2COH$	 $MeO{-}Si(Me)_2OCMe_2Ph$	Addition products	
					$Me_3SiO\cdot$	$PhMe_2CO\cdot$
n-Nonane [a]	0.67	0.48	0.19	0.3	absent	absent
α-Methylstyrene	0.08	0.48	0.11	0.27	0.65	0.14
Styrene	0.11	0.47	0.05	0.27	0.83	not determined
Tri-isobutylene	0.35	0.5	0.2	0.3	0.35	absent
Cyclohexene	0.65	0.26	0.54	0.22	0.12	absent
1,1-Diphenylethylene	0.02	0.65	absent	0.07	0.9	0.28

[a] These data are listed for comparison.

$$R_3EOOR' + SH \rightarrow R_3EOH + R'O\cdot + S\cdot \quad (3)$$

We have found that in olefins the decomposition of these peroxides proceeds quite differently. In this case the complexing of organoelement peroxide with olefin occurs, which facilitates the decomposition of a peroxide compound. The investigated compounds (I—V) were trimethyl(t-butylperoxide)silane, trimethyl(cumylperoxy)silane, triethyl(t-butylperoxy)germane, triethyl(t-butylperoxy)tin and triethyl(cumylperoxy)tin, respectively. Olefins, 1-heptene, cyclohexene, styrene, α-methylstyrene, 1,1-diphenylethylene, 2,3-dimethylbutadiene-1,3, tri-isobutylene and anethole were used.

Experimental

The organoelement peroxides were obtained by described procedures [4,5]. The purity of the peroxides in all cases is close to 100%. The peroxide decomposition was carried out by the ampoule method in the absence of air oxygen [2]; peroxide oxygen was analyzed by the procedures described earlier [6].

The peroxide decomposition products were analyzed by gas-liquid chromatography using chromatograph "Tsvet-104" with the katharometer. Carrier gas was helium. The separation was carried out using steel columns (100 × 0.4 cm) filled with SE-30 (5%) on the Chromatone N-AW-HMDS (0.2—0.25 mm) or Reoplex 400 (15%) on the same support. The column temperature was varied from 60—220°C.

The thermochemical measurements were made using an adiabatic calorimeter according to the described procedure [7]. The mixing of components was performed in a dry nitrogen atmosphere at 298.15 K. Under such conditions the peroxides investigated did not undergo decomposition in the solutions of the substances studied over a long period. The error in determining enthalpies of mixing was 10—20 cal mol^{-1}.

$R_3EO\cdot$ radicals were obtained by peroxide decomposition (for I—V) as well as by decomposition of $Me_3SiOOSiMe_3$, $Et_3SiOOCMe_3$ and $Me_3GeOOCMe_3$ under UV-irradiation ($\lambda = 253.7$ nm), the absorption of which by the peroxides investigated is characterized by rather high extinction coefficients.

Results and discussion

In the olefin the peroxide decomposition, with an extent of reaction 50—90%, follows first order kinetics. The olefins suppress the induced peroxide decomposition [8]. The extent of this depends upon the nature of the initial substrate and the olefin content in the reaction mixture. The kinetic and activation parameters of the peroxide decomposition (for I—V) are listed in Table 1. The main products of $Me_3SiOOCMe_2Ph$ decomposition in olefins are given in Table 2. The formation of products such as Me_3SiOH, the ketone and alcohol indicates that most of the peroxide (70—93%) decomposes homolytically in olefins. It follows from Table 1 that the rate constants of peroxide decomposition (for I—V) are higher in olefins, but activation energy is lower than in n-nonane (the entropy of activation is negative).

From the kinetic data, it is supposed that the primary reaction of peroxide decomposition (for I—V) in olefins is an equilibrium reaction of complexing peroxide with olefin (eq. 4). The interaction of the peroxides studied with

$$R_3EOOR' + X_2C{=}CY_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [R_3EOOR'\cdot X_2C{=}CY_2] \qquad (4)$$

olefins is confirmed by the thermochemical data. In this work the enthalpies of mixing triethyl(t-butylperoxy)tin (IV) with n-nonane, cyclohexene, styrene, 1,1-diphenylethylene, 2,3-dimethyl-1,3-butadiene, phenylacetylene, methylmethacrylate and pyridine were determined over a wide range of concentrations, and also IV—triethylamine and IV—chloroform in the ratio of components 1 : 1 and 1 : 2, respectively. The enthalpies of mixing peroxides I, III, V as well as those of triethyl(triethylstannyloxy)tin (VI) and triethyl(ethoxy)tin (VII) with chloroform, pyridine and some olefins were also estimated in the ratio 1 : 1 and 1 : 2 (peroxide : solvent), respectively (Table 3). To evaluate the relative basicities of some olefins used in the work, the enthalpies of mixing them (1 : 2) with $AsCl_3$ were determined.

The values of enthalpies of mixing peroxide IV with olefins and pyridine are negative in the whole range of the solution concentrations. Maximum heat liberation is obtained with the composition 1 : 1. The enthalpies of mixing peroxide IV with n-nonane are positive. These data are only valid for complexing the peroxide IV with olefins and pyridine (Fig. 1).

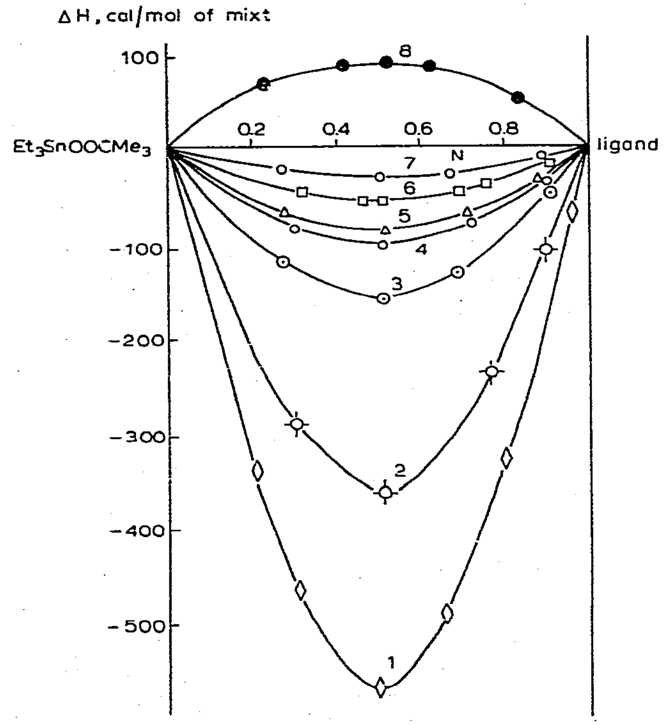


Fig. 1. The enthalpies of mixing triethyl(t-butylperoxy)tin with pyridine (1), phenylacetylene (2), 2.3-dimethyl-1,3-butadiene (3), methylmethacrylate (4), styrene (5), 1,1-diphenylethylene (6), cyclohexene (7) and n-nonane (8) at 298.15 K.

TABLE 3

ENTHALPIES OF MIXING FOR SOME ORGANOELEMENT COMPOUNDS WITH ORGANIC SOLVENTS (in cal mol^{-1} of organoelement compound, ratio of components 1 : 1, T = 298.15 K)

OEC	Solvent				
	C_5H_5N	Et_3N	$Ph_2C{=}CH_2$	$CHCl_3$ [a]	PhC≡CH
I	+180			−910	+20
III	+200			−1570	
IV	−1150	−140	−110	−2650	−740
V	−1700		−200	−2510	
VI	+740		+170	−4030	−1040
VII	−170	+730	+1060	−2670	−2000

[a] The ratio of components is 1 : 2 (OEC : solvent).

Olefin complexes with various compounds have been described earlier and are at present widely studied [9,10]. It is of interest to note that with increasing olefin basicity the absolute values of the enthalpies of mixing peroxide IV and $AsCl_3$ increase (the enthalpies of mixing $AsCl_3$ with cyclohexane, 1-heptene, cyclohexene, phenylacetylene, 1,1-diphenylethylene, 2,3-dimethyl-1,3-butadiene, in the ratio of components 2 : 1 were +400, −450, −540, −620, −1400 cal mol^{-1} of $AsCl_3$, respectively, at 298.15 K.

From the enthalpies of mixing peroxide IV with olefins and pyridine in various ratios, the stability constants C_s and the enthalpies of formation of complexes were calculated at 298.15 K (Table 4). In the calculations performed by the described procedure [11] the enthalpies of "physical" mixing of components were taken into account.

Based on the initial rate dependence of the decomposition of IV upon the composition of peroxide—1,1-diphenylethylene (DPE) mixture in n-nonane, the stability constants (C_s, l mol^{-1}) of peroxide (IV)—DPE complexes were determined by the molar ratio method, which proved to be equal to 0.042 at 413 K and 0.038 at 433 K.

The complexing ability of peroxides IV and V is due to an electron-acceptor character of the peroxide group. This is observed in comparing the enthalpies of mixing the peroxides indicated with organotin esters VI and VII (Table 3). In mixtures with pyridine, triethylamine and DPE, the enthalpies of mixing peroxides IV and V are less than the corresponding values for the esters. The values for esters are usually positive. On the other hand, the electron-donor ability of the same peroxides is weaker in mixtures with chloroform and phenylacetylene when compared with organotin esters (Table 3). The difference in the enthalpies of mixing peroxides IV and V with the compounds studied (Table 3) may be explained by a stronger acceptor influence of the cumylperoxy group than that of the t-butylperoxy fragment of peroxide IV.

It is seen from Table 3 that the enthalpies of mixing organosilicon and organogermanium peroxides are positive even with the strongest donor solvent studied, viz. pyridine. It points to a smaller complexing ability of peroxides I and III with electron-donors. Also, it indicates that the ligand coordination is likely to occur through a heteroatom and not through a peroxide bond. Otherwise, the acceptor ability of organosilicon and organogermanium peroxides should

TABLE 4

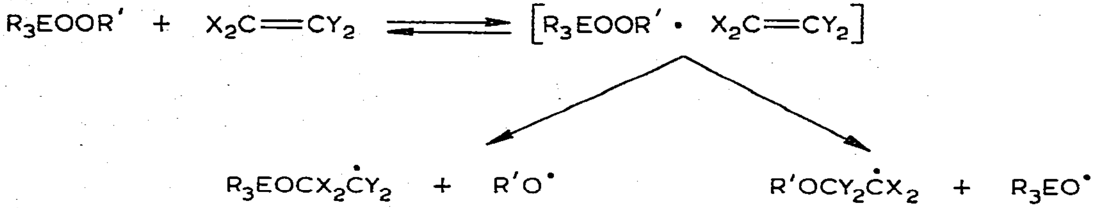
STABILITY CONSTANTS (C_S, l mol^{-1}) AND ENTHALPIES OF FORMATION (ΔH, cal mol^{-1}) OF PEROXIDE IV—LIGAND COMPLEXES AT 1 : 1 COMPOSITION

	Cyclohexene	1-1-Diphenyl ethylene	Styrene	Methylmethacrylate	2,3-Dimethylbutadiene-1,3	Phenyl acetylene	Pyridine
$-\Delta H$	1670	2720	2580	2460	2520	2890	3850
C_S	0.054	0.055	0.052	0.059	0.084	0.168	0.184

be much higher because of d_π—p_π conjugation of the heteroatom with a peroxide oxygen. The latter fact is an explanation for decreasing donor ability of a peroxide group, relative to chloroform and phenylacetylene, when passing from organotin peroxide to the organosilicon analogue.

The composition of the products of decomposition of organoelement peroxide of the silicon subgroup (e.q., peroxide II, Table 2) in olefins indicates that the complex formation of peroxide with olefin facilitates the peroxide substrate decomposition through the homolytical mechanism (Scheme 1).

SCHEME I



The orgniac and organoelement radicals undergo competitive addition reactions towards an olefin multiple bond and reactions via hydrogen abstraction.

We have studied the competition of these reactions exemplified by organoelement oxyradicals $R_3EO\cdot$ (where E is Si, Ge or C and R is Me, Et and Ph) as well as by a number of olefins such as 1-hexene, 1-heptene, 1-nonene, cyclohexene and 2,3-dimethyl-1,3-butadiene. The radicals were obtained by the decomposition of peroxides I—V, $Me_3SiOOSiMe_3$, Et_3SiOOt-Bu, $Me_3GeOOCMe_3$ under UV-irradiation.

It is known that UV-irradiation gives rise to photo-dissociation of peroxides with cleavage of the weakest peroxide bond [12] (eq. 5). The subsequent

$$R_3EOOR' \xrightarrow{h\nu} R_3EO\cdot + R'O\cdot \qquad (5)$$

reactions of oxyradicals determine the composition of the final products.

On the photolysis of organo-silicon and -germanium peroxides in n-nonane only 1 mole of trialkyl(aryl)silicon hydroxide (or 0.5 mole of hexaalkyldigermanoxane) and 1 mole of tertiary alcohol are formed per mole of peroxide decomposed, which are products of hydrogen abstraction reaction from solvent molecules by the corresponding oxyradicals (eq. 6—8).

$$R_3EO\cdot + SH \xrightarrow{k_0} R_3EOH + S\cdot \tag{6}$$

$$R'O\cdot + SH \rightarrow R'OH + S\cdot \tag{7}$$

$$2\ R_3GeOH \rightarrow R_3GeOGeR_3 + H_2O \tag{8}$$

We have found that the quantum yield of peroxide photo-decomposition in n-nonane and olefins is within 0.9—0.95 at concentrations of 0.05—0.1 mol l^{-1} and does not depend on the nature of the solvent or temperature. These facts and the nature of the products analyzed indicate the absence of the induced decomposition of peroxides under the above-mentioned conditions.

In olefins the addition of oxyradicals occurs about a multiple bond in parallel with the hydrogen abstraction reactions (eq. 9).

$$R_3EO\cdot + X_2C{=}CY_2 \xrightarrow{k_n} R_3EOCX_2\dot{C}Y_2 \tag{9}$$

The quantitative characteristic of the relative oxyradical reactivity is a ratio of the rate constants of elementary addition reactions and hydrogen abstraction reactions, which is equal to the product concentration ratio of these reactions in the absence of the peroxide induced decomposition and the reaction product influence. The values of k_n/k_0 have been determined for the decomposition of

$$k_n/k_0 = C_{R_3EOCX_2CY_2}/C_{R_3EOH}$$

organo-silicon and -germanium peroxides in some olefins.

As can be seen from Table 5 the nature of the substituents at a heteroatom essentially does not affect the ratio k_n/k_0. The substitution of three methyl groups by phenyl in the group R_3SiO did not change the ratio between k_n and k_0 within the experimental error. $R_3GeO\cdot$ radicals behave similarly. Steric hindrances are not likely to influence substantially the competition between addition and hydrogen abstraction reactions.

The probability of the addition reaction of $R_3EO\cdot$ with an olefin double bond depends strongly on the nature of the heteroelement. It decreases to zero in the series: $Me_3SiO > Me_3GeO > Me_3CO$. The ability to react via hydrogen abstraction reaction increases in the same series. In examining the relative arrange-

TABLE 5

DEPENDENCE OF k_n/k_0 ON THE NATURE OF THE $R_3EO\cdot$ RADICAL AND SOLVENT (T = 25°C, C_0 = 0.1 mol l^{-1})

Radical	k_n/k_0					
	n-Nonane	1-Nonene	1-Heptene	1-Hexene	Cyclo-hexene	2,3-Dimethyl-butadiene-1,3
$Ph_3SiO\cdot$	0	0.69	1.74			
$Et_3SiO\cdot$	0	0.69	1.72	1.74	1.0	24.0
$Me_3SiO\cdot$	0		1.83			
$Et_3GeO\cdot$	0		0.43		0.43	22.0
$Me_3GeO\cdot$	0		0.37			
$Me_3CO\cdot$	0	0	0	0	0	0.2
$PhMe_2CO\cdot$	0	0	0	0	0	1.0

ment of molecular orbitals of the olefin and oxyradical [13] one can suppose that the addition reaction will be favourable for the $R_3SiO\cdot$ radical as the energy of R_3SiO molecular orbital occupied by an unpaired electron will be closer to that of an upper occupied molecular orbital of olefins such as 1-hexene, 1-heptene, 1-nonene, cyclohexene and much lower than that of molecular orbital of 2,3-dimethyl-1,3 butadiene. The probability of the addition reactions to the latter olefin increases appreciably.

The addition of radicals to olefins depends strongly on the nature of the olefin. For $Et_3SiO\cdot$ radical the ratio k_n/k_0 decreases regularly in the series: 1-hexene > 1-heptene > 1-nonene, as increasing the number of methylene groups raises the probability of the hydrogen abstraction reaction. The effect of changing the alkoxy groups is minimal in the addition of the radicals to reactive 2,3-dimethyl-1,3-butadiene.

The temperature affects substantially the competitive ability of the addition and hydrogen abstraction reactions. From temperature dependence of the ratio k_n/k_0 the difference in the activation energy of the competitive reactions ($E_0 - E_n = 1.5$ kcal mol^{-1}) and the ratio of the corresponding pre-exponents ($k_n^0/k_0^0 = 15.0$) were determined. The activation energy of the hydrogen abstraction reaction by $Me_3SiO\cdot$ radical is 1.5 kcal mol^{-1} more than that of the addition reaction. Therefore, with increasing temperature the probability of the addition reaction of $R_3EO\cdot$ radical decreases and the abstraction reaction predominates over the addition reaction.

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