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THERMODYNAMIC PROPERTIES OF SILICON CONTAINING ACETYLENE PEROXIDES

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Abstract. A technique for the explosion combustion of liquid organosilicon peroxides has been developed. Five silicon containing acetylene peroxides have been investigated thermodynamically. Their combustion and evaporation enthalpies have been determined. Formation enthalpies of the compounds concerned in the condensed and gaseous states have been calculated. The magnitudes of two fragments for Benson additive scheme of formation enthalpies have been determined.

Key words: organosilicon peroxides, evaporation enthalpy, formation enthalpy, saturated vapour pressure, fragment for Benson additive scheme.

1. Introduction

Organosilicon peroxides possess the whole range of valuable properties. Their high thermal stability, hydrophobic qualities, hydrolytic, and storage stabilities have to be mentioned separately. Various free-radical processes, such as vulcanization of elastomers, high temperature (420–570 K) initiation of polymerization, polymers modification, and varnish compositions curing [1] are the major fields the above mentioned compounds are used. In addition to that, film-forming abilities, antioxidant properties, and biological activity of the silicon containing acetylene peroxides are being investigated [2].

Absence of the thermodynamic properties of the mentioned compounds complicates the processes of their synthesis and inculcation.

The results of the experimental determination of the formation enthalpies of the five liquid silicon containing acetylene peroxides in the condensed and gaseous states are represented in this article. The following five compounds had been the subjects of the investigation:

3-methyl-3-tert-butylperoxy-1-trimethylsilyl-1-butyn (I)
$(CH_3)_3COOC(CH_3)_2C \equiv CSi(CH_3)_3$

3-methyl-3-tert-amylperoxy-1-trimethylsilyl-1-butyn (II)
$CH_3CH_2(CH_3)_2COOC(CH_3)_2C \equiv CSi(CH_3)_3$

3-methyl-3-tert-hexylperoxy-1-trimethylsilyl-1-butyn (III)
$CH_3(CH_2)_2(CH_3)_2COOC(CH_3)_2C \equiv CSi(CH_3)_3$

3-methyl-3-[2-cyclohexylpropylperoxy]-1-trimethylsilyl-1-butyn (IV)
$cyclo\text{–}C_6H_{11}(CH_3)_2COOC(CH_3)_2C \equiv CSi(CH_3)_3$

dimethyldi[3-methyl-3-tert-amylperoxy-1-butynyl]silan (V)
$[CH_3CH_2(CH_3)_2COOC(CH_3)_2C \equiv C]_2Si(CH_3)_2$

2. Experimental

2.1. Synthesis

Samples of the studied peroxides have been synthesized according to the procedure [3]. All the compounds have been purified by vacuum distillation. The products have been identified by infrared spectroscopy (spectrometer UR-20), nuclear magnetic resonance spectroscopy (spectrometer Tesla BS-567A), and ultraviolet spectroscopy (spectrometer Specord UV-Vis). The contents of carbon, silicon, and hydrogen have been established using an element analysis. The content of active oxygen has been estimated by the iodine method. The molecular masses of the samples have been obtained by the cryoscopy method.

2.2. Purity

The purity of the compounds has been measured by high pressure solution chromatography method. A device for measuring the purity of the compounds consisted of the pump, ultraviolet and refractometric detectors and Separon SGX CN column. Eluent: a mixture of heptan-isopropanol (98:2 volume parts ratio). The content of the major component has been not less than 99.2 % for all the studied compounds. The thermal properties of the peroxides have been studied at the Paulik-Paulik-Erday derivatograph. Maximum destruction temperature has been 430–440 K.

2.3. The sublimation enthalpies

The vapor pressure of the silicon containing acetylene peroxides has been measured by integral effusion Knudsen method. A stainless steel chamber with the

following parameters has been utilized in the experiments: 10 mm diameter, 20 mm height, 1 mm wall thickness. Two membranes made of 0.05 mm thick nickel foil have been used. The diameters of the effusion apertures have been 0.5903 mm and 0.3247 mm. The design of the experimental device has been taken from [4]. The experimental techniques have been chosen based on the recommendations [5].

The reliability of the device functioning has been proved by measuring benzoic acid vapour pressure in the temperature interval of 318–348 K. The results of the measuring have been processed using the least-squares method with the Studentized confidence coefficient of 95 per cent and represented as a set of linear equations:

$$\ln P_C=(34.8\pm0.4)-(111.1\pm1.3)\times10^2T^{-1} \quad (1)$$

For the membranes with 0.5903 mm apertures.

$$\ln P_C=(35.0\pm0.5)-(111.5\pm1.5)\times10^2T^{-1} \quad (2)$$

For the membranes with 0.3247 mm apertures

The sublimation enthalpies have been calculated according to equations (1) and (2) and equal 92.4±1.1 and 92.7 ±1.3 kJ·mol^{-1} respectively. These values are within experimental error and are consistent with those previously published [6].

The saturated vapour pressure of the benzoic acid has been calculated by extrapolation of the values of the vapour pressure inside the chamber with different aperture diameters to zero diameter [7]. Adjustment multipliers for membranes with the diameters of 0.3247 mm and 0.5903 mm equal 1.04 and 1.14 respectively. These coefficients have been later used for calculation of saturated vapour pressure of silicon containing acetylene peroxides.

A series of 7 to 15 experiments have been conducted for every compound. The results of the experiments could have been easily distorted by the presence of volatile impurities. Therefore, the results of the experiments had not been considered until the rate of evaporation became constant (±1 per cent) under the predetermined temperature. The error of the vapour pressure measuring which can be brought by non-volatile impurities is less than the measuring accuracy.

The mass of the effused compound Δm has been determined by weighting of the effusion chamber with the precision of $\pm5\cdot10^{-6}$ g. The temperature of liquid thermostat has been adjusted to an error of ±0.1 K. The precision of measuring the temperature T and duration of effusion τ was ± 0.05 K and ±1 s respectively.

The results of the effusion measuring of the studied peroxides including saturated vapour pressure P, and vapour pressure inside the chamber P_C, are presented in Table 1.

Approximation equation coefficients of the temperature dependencies of the saturated vapour pressure $lnP = A+B/T$ and average evaporation enthalpies $\Delta_l H$ in the investigated range of temperatures ΔT are presented in Table 2. Here ρ is a correlation coefficient.

2.4. The combustion enthalpies

The combustion enthalpies of the silicon containing acetylene peroxides have been measured by a water calorimeter B-08 MA equipped with a isothermal (± 0.03 K) jacket. Energy equivalent of the calorimetric system W has been estimated by the combustion of the standard benzoic acid with the content of the major component being equal to 99.995 mol per cent, the estimation precision being equal to ± 0.06 per cent.

The combustion heat of the benzoic acid allowing for the Jessup factor was equal to 26426.9 J·g^{-1}. The initial pressure of the oxygen which has been previously cleaned from the combustible impurities, carbon dioxide and water was equal to $29.4\cdot10^5$ Pa. The initial temperature of the main period in all experiments has been 298.15 K.

The choice of the combustion technique for the liquid organosilicon peroxides has been made after experimenting on the compound V. The combustion has been held using a platinum or quartz crucible or a platinum net. The maximum combustion completeness of the compound V has been attained by using a platinum crucible and has been equal to 99.1–99.8 per cent. Therefore, a platinum crucible has been used for all other compounds under study.

The samples have been isolated in double terylene containers before the combustion. In addition to being an isolation terylene has also been an auxiliary substance in the combustion. It has enabled to attain simultaneous ignition across the whole surface of the sample, increase the temperature in the combustion zone, as well as to ensure completeness of combustion and prevent formation of a silicone carbide [8]. A cotton thread has been used for the ignition of the samples.

A quantitative analysis of the combustion products aimed at establishing the presence of carbon oxide, carbon dioxide, soot, and nitric acid has been carried out after every combustion. The quantity of the carbon dioxide has been measured by the Rossini method [9] with the precision of $\pm2\cdot10^{-4}$ g. Reliability of the gas analysis has been proved by the series of experiments with combustion of standard benzoic acid. The content of carbon oxide in the combustion products has not exceeded the precision of the gas analysis. The amount of soot formed on the walls of the platinum crucible has measured by weighting with a precision of $\pm5\cdot10^{-6}$ g.

Corrections for the combustion of the terylene container (Q_C), the cotton thread (Q_{Th}), as well as for the combustion of the soot to carbon dioxide (Q_S), and formation of the nitric acid (Q_A) have been made to calculate combustion heats of the compounds. The following combustion energies in the bomb conditions (J·g^{-1}) have been used in the calculations: terylene 22944.2 [10]; cotton thread 16704.2 [11]; soot to carbon dioxide 32800 [12]; formation of nitric acid 59 kJ·mol^{-1} [9]. The

Table 1

The results of the experimental determination of temperature dependencies of vapour pressure of the studied peroxides

τ, s	$\Delta m \cdot 10^3$,g	T, K	P_C, Pa	P, Pa	τ, s	$\Delta m \cdot 10^3$,g	T, K	P_C, Pa	P, Pa
Peroxide I					Peroxide III				
2436	8.545	277.6	12.33	12.82	2479	3.500	287.1	4.290	4.462
2437	8.245	277.6	11.87	12.34	2750	4.165	289.1	5.120	5.325
2437	9.310	278.7	13.44	13.98	2749	4.900	291.1	6.047	6.289
2437	9.920	279.5	14.34	14.91	2749	5.875	293.0	7.276	7.567
2436	10.625	280.4	15.39	16.01	2754	7.120	295.1	8.832	9.185
2437	10.505	280.4	15.21	15.82	2749	8.475	297.0	10.57	10.99
2437	11.320	281.2	16.43	17.09	1850	6.100	297.9	11.24	11.69
2437	12.190	282.1	17.70	18.41	Peroxide IV				
2437	13.160	283.0	19.15	19.92	3628	1.705	307.2	1.524	1.585
2437	14.200	283.9	20.70	21.53	3628	2.055	309.1	1.841	1.915
2437	15.215	284.8	22.19	23.08	2728	1.865	311.1	2.232	2.321
2437	15.955	285.6	23.33	24.26	2728	2.245	313.2	2.694	2.802
2437	16.845	286.4	24.65	25.64	1828	1.720	314.7	3.088	3.212
2437	17.560	287.1	25.75	26.78	2728	2.480	314.6	2.986	3.105
Peroxide II					2733	2,790	315,7	3,356	3.490
2436	3.870	277.6	5.419	5.636	2728	3.180	317.2	3.841	3.995
2437	4.115	278.7	5.771	6.002	Peroxide V				
2435	4.085	278.7	5.737	5.966	3624	0.790	318.2	0.177	0.202
2436	4.510	279.7	6.329	6.582	3625	0.780	318.0	0.174	0.198
2436	4.980	280.8	6.993	7.273	3621	1.295	323.1	0.293	0.334
2436	5.295	281.9	7.453	7.751	3620	1.340	323.1	0.303	0.345
2135	5.135	283.0	8.294	8.626	3622	2.235	328.0	0.508	0.579
2437	6.600	284.1	9.344	9.718	3021	1.860	328.0	0.507	0.578
2436	7.190	285.2	10.19	10.60	3620	2.175	328.0	0.495	0.564
2437	7.795	286.2	11.07	11.51	2721	2.725	333.1	0.831	0.947
2436	8.500	287.2	12.10	12.58	2721	2.640	333.0	0.805	0.918
2435	9.255	288.2	13.20	13.73	1822	3.030	338.0	1.391	1.586
2435	10.210	289.2	14.58	15.16	1821	2.930	338.0	1.346	1.534
2435	11.170	290.2	16.00	16.64					
2435	12.110	291.2	17.35	18.04					

Table 2

Approximation equation coefficients of the temperature dependencies of the saturated vapour pressure and evaporation enthalpies of the studied peroxides

Peroxide	ΔT, K	A	$-B \cdot 10^{-2}$, K	ρ, per cent	$\Delta_V H$, kJ·mol^{-1}
I	277–287	25.7 ± 0.7	64.4 ± 1.9	99.93	53.5 ± 1.6
II	277–292	27.1 ± 0.6	70.5 ± 1.8	99.92	58.7 ± 1.5
III	287–298	28.5 ± 0.8	77.5 ± 2.2	99.98	64.4 ± 1.9
IV	307–318	29.5 ± 0.8	89.2 ± 2.4	99.94	74.2 ± 2.0
V	318–338	33.2 ± 0.6	110.7 ± 1.9	99,99	92.0 ± 1.6

Table 3

Results of the calorimetric determination of combustion energies of the studied peroxides

m, g	ΔT, V	Q_Σ, J	Q_{Th}, J	Q_C, J	Q_A, J	Q_S, J	k, %	$-\Delta U_B$, J·g^{-1}
1	2	3	4	5	6	7	8	9
Peroxide I W=14939.3 J·V^{-1}								
0.165110	0.4949	7393.46	39.25	1039.03	1.18	8.20	99.56	38459.5
0.163470	0.4837	7226.14	35.16	968.36	1.77	6.07	99.33	38349.2
0.183040	0.5391	8053.78	34.08	1020.21	1.77	6.56	99.52	38450.6
0.161895	0.4822	7203.73	31.74	974.21	2.36	9.84	99.87	38378.8
0.148430	0.4566	6821.28	36.25	1010.92	1.77	9.84	99.95	38370.5
0.137905	0.4237	6329.78	39.25	1037.08	1.77	8.20	99.42	38363.3
0.128665	0.4007	5986.18	33.41	1027.90	1.77	4.92	99.55	38474.0
Peroxide II W=14930.5 J·V^{-1}								
0.128540	0.4371	6526.12	143.74	1402.46	8.26	—	99.49	38875.3
0.115450	0.4096	6115.53	145.49	1495.39	3.54	—	99.49	38921.9
0.135395	0.4538	6775.46	136.81	1402.69	3.54	—	99.59	38802.8
0.113070	0.4023	6006.54	122.19	1510.42	1.77	—	99.66	38799.9
0.166295	0.5092	7602.61	49.61	1081.25	1.18	8.86	100.00	38962.0
0.168735	0.5086	7593.65	53.54	973.87	1.48	4.59	99.79	39013.2
0.163480	0.4920	7345.81	44.68	967.10	1.18	8.86	100.00	38788.1
0.168150	0.5052	7542.89	40.51	999.45	1.48	10.66	99.24	39028.4
0.154185	0.4680	6987.47	42.93	960.90	1.18	5.25	99.72	38943.8
0.132215	0.4162	6214.07	38.59	1042.24	1.48	3.61	99.72	38946.0
0.161785	0.4876	7280.11	39.25	973.64	1.18	4.43	99.95	38776.7
Peroxide III W=14939.3 J·V^{-1} (exp. 1, 2, 5, 6); W=14930.5 J·V^{-1} (exp.3, 4)								
0.163585	0.5012	7487.58	34.24	1072.64	1.77	3.28	99.23	39317.6
0.143260	0.4461	6664.42	38.42	1032.49	1.77	4.92	99.47	39273.8
0.139700	0.4637	6923.27	112.80	1360.82	1.77	—	99.00	39394.7
0.116295	0.4000	5972.20	106.14	1333.29	1.18	—	99.03	39353.8
0.124585	0.3993	5965.26	34.74	1064.73	0.59	10.99	99.58	39305.0
0.127870	0.4098	6122.13	43.01	1085.26	0.59	8.20	99.36	39365.1
Peroxide IV W=14930.5 J·V^{-1} (exp. 1-4); W=14939.3 J·V^{-1} (exp. 5-8)								
0.115280	0.3995	5964.73	116.08	1274.55	3.54	—	99.70	39769.5
0.122200	0.4046	6040.88	53.62	1161.78	1.77	12.63	99.37	39828.3
0.120280	0.4051	6048.35	49.78	1217.88	1.77	11.81	99.95	39844.2
0.092580	0.3318	4953.94	65.81	1203.19	1.18	11.15	100.00	39810.6
0.158190	0.4839	7229.13	45.10	930.39	2.36	8.20	99.55	39748.9
0.137450	0.4368	6525.49	37.58	1063.46	2.36	6.56	99.42	39726.2
0.143495	0.4450	6647.99	38.42	934.98	2.36	6.56	99.72	39685.9
0.108025	0.3533	5278.05	42.60	970.54	1.77	9.84	99.49	39759.0
Peroxide V W=14930.5 J·V^{-1}								
0.098340	0.3292	4915.12	60.89	1186.67	2.36	16.73	99.59	37587.4
0.111095	0.3580	5345.12	63.73	1148.59	2.36	15.42	99.42	37531.1
0.110580	0.3552	5303.31	71.41	1113.83	2.36	15.25	99.59	37511.2
0.095815	0.3150	4703.11	73.50	1049.12	1.77	9.02	99.73	37545.5
0.107615	0.3552	5303.31	68.65	1227.17	2.36	12.63	99.49	37531.9
0.103725	0.3270	4882.27	59.63	953.91	2.36	11.81	99.51	37579.4
0.109440	0.3428	5118.18	62.97	966.75	1.77	17.38	99.79	37574.6

Table 4

Energies of combustion and enthalpy characteristics of the studied peroxides

Peroxide	$-\Delta_C U^o_{298.15\,K}$	π	-ΔnRT	$-\Delta_C H^o_{298.15\,K}$	$-\Delta_f H^o_{298.15\,K}$ (liquid)	$-\Delta_f H^o$(gas) exp.	$-\Delta_f H^o$(gas) calc.
	kJ·mol^{-1}						
I	8770 ± 11	2	15	8785 ± 11	307 ± 11	254 ± 11	249
II	9427 ± 15	3	16	9443 ± 15	328 ± 15	269 ± 15	269
III	10085 ± 12	3	17	10102 ± 12	348 ± 12	284 ± 12	290
IV	11789 ± 13	4	20	11809 ± 13	393 ± 13	319 ± 13	318
V	14889 ± 11	6	22	14912 ± 11	402 ± 11	310 ± 11	310

quantity of the carbon dioxide which has formed from the combustion of 1 g of terylene and the cotton thread is 2.2872 g and 1.6284 g respectively. The combustion energies ΔU_B determination results for the studied peroxides are represented in Table 3. Here, m is a mass of the initial sample; ΔT is an actual temperature rise; Q_Σ is a total quantity of the emitted energy, k is combustion completeness.

Calculation of standard combustion enthalpies $\Delta_C H^0_{298.15\,K}$ of silicon containing acetylene peroxides has been based on the combustion energy values of the peroxides including Washburn correction π and correction for the variation in the number of moles of gas ΔnRT. The calculation of formation enthalpies in condensed phase has been based on the following key values of $\Delta_f H^0_{298.15\,K}$, kJ·mol^{-1}: –285.830 ± 0.042 (H_2O, liq.), –393.514 ± 0.046 (CO_2, gas) [13]; –939.39 ± 0.52 (SiO_2, am. hydr.) [8].

The results of the calorimetric determination of standard energies and enthalpies of combustion and formation of silicon containing acetylene peroxides are represented in Table 4. A standard deviation of average values has been calculated taking into account the Studentized confidence coefficient of 95 per cent.

3. Results and Discussion

Reaching a high degree of combustion completeness is a major difficulty in determining a heat of silicon containing peroxides formation heat. This problem appears at the very beginning of the process; the first portions of the newly formed silicone dioxide either envelop or sorb the substance being burned, thus preventing access for oxygen and combustion ceases [8].

As a result of burning of the studied organosilicon peroxides all inner surface of the bomb has been covered with a silicon dioxide powder. This reconfirms that the burning process included an explosion. Evidently, the compound has dispersed into droplets during the explosion. These droplets have burned out failing to reach the cold walls of the bomb. The combustion completeness of all the studied peroxides in all the experiments exceeded 99 per cent, which is considered to be sufficient for this class of compounds.

To calculate formation enthalpies of silicon containing compounds from the enthalpies of their combustion in oxygen, a reliable value of a standard formation enthalpy of hydrated amorphous silicon dioxide is needed. The values used up to now have ranged from –850.77 to –939.39 kJ·mol^{-1} [8, 14-16]. We have chosen the value of $D_f H^0_{298.15\,K}(SiO_2)$ to be equal –939.39 ±0.52 kJ·mol^{-1}. It has been obtained by direct combustion of the silicon (purity equal to 99.999 per cent) [8] and reconfirmed by reaction calorimetry [17].

The analysis of the obtained results (see Tables 2 and 4) shows that absolute values of the enthalpies of evaporation and formation in liquid and gaseous phase (kJ·mol^{-1}) are increasing in the homologous series of compounds I-III by 5, 21, and 15 respectively. The contribution of C-$(C)_2(H)_2$ fragment in the listed above enthalpy characteristics (kJ·mol^{-1}) is 4.8 [7]; 24 [18] and 20 [19] respectively. Therefore, the values of the enthalpy characteristics increase are equal to those of corresponding enthalpies of C-$(C)_2(H)_2$ fragment within the precision of determination. The differences between the fragments of methyl and cyclohexyl groups (kJ·mol^{-1}) for compounds I and IV are equal: for gaseous phase formation enthalpies –68.1 [19], for liquid phase formation enthalpies – 82.3 [18], and for evaporation enthalpies 25.1 [7]. These values also correspond to the results of the experiments within the precision of determination: –65, –86 and 20.7 kJ·mol^{-1} respectively (see Tables 2 and 4). The obtained results prove the additivity of enthalpy characteristics of the studied silicon containing peroxides.

The studied compounds contain fragments whose enthalpy characteristics have not been studied yet. That is why, due to insufficient data fragments for calculation of liquid phase formation enthalpies and evaporation enthalpies can not be determined.

Gaseous phase formation enthalpies of the fragments have been taken mostly from [19]. The fragments O-(C)(O) – 19.32 kJ·mol^{-1} and C-$(O)(C)_2(Ct)$ – 9.55 kJ·mol^{-1} have been taken from [20]. The first fragment has been determined on the base of the formation enthalpies of over fifty peroxides, the second one was determined on the base of five compounds with a triple bound. The value of C-$(Si)(H)_3$ fragment (kJ·mol^{-1}) can be found in the following articles: [21] –44.27; [22-24] –40.27; [25] –42.17. All the fragments of organosilicon compounds have been recalculated [21-24]. Therefore, we have chosen the value of –42.17 kJ·mol^{-1}. It is equal to the value of the fragment C-$(C)(H)_3$ [19].

The system of four identic equations has been derived by inclusion of the known fragments into the equations of formation enthalpies of the compounds I – IV. Solution of this system of equations has allowed to calculate a group contribution $(C_t) \equiv CSi(C)_3$ which is equal to 49 kJ·mol^{-1}. The value of $[(C_t)\equiv C]_2Si(C)_2$ fragment 159 kJ·mol^{-1} has been determined from the formation enthalpy of the compound V.

The calculated values of formation enthalpies belong to the confidence interval of the experiment (Table 4).

4. Conclusions

The magnitudes of two fragments for Benson additive scheme allow calculate the formation enthalpies of silicon compounds, which contain determined fragments.

The obtained base thermodynamic characteristics of organosilicon peroxides can be used for optimization of existing and creation of new technologies of synthesis and purification of elementorganic peroxides.

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ТЕРМОДИНАМІЧНІ ВЛАСТИВОСТІ КРЕМНІЙВМІСНИХ АЦЕТИЛЕНОВИХ ПЕРОКСИДІВ

Анотація. *Розроблено методику спалювання рідких кремнійорганічних пероксидів із вибухом. Термодинамічно досліджені п'ять кремнійвмісних ацетиленових пероксидів: визначені ентальпії згоряння та випаровування. Розраховані ентальпії утворення сполук в рідкому і газоподібному стані. Розраховані два фрагменти до адитивної схеми Бенсона для визначення ентальпій утворення.*

Ключові слова: *кремнійорганічні пероксиди, ентальпія випаровування, ентальпія утворення, тиск насиченої пари, фрагмент адитивної схеми Бенсона.*