Calculation of Activation Volumes of Thermal Conversions of Trimethylsilyl(cumyl) Peroxide by the Spline Approximation Method

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Abstract—The overall rate constants k_s of thermal conversions of trimethylsilyl(cumyl) peroxide (TMSCP) at pressures P up to 10 kbar are separated into components taking into account the ratios of the corresponding products: the rate constants of radical decomposition k_d and the rate constant of rearrangement k_r. Spline approximation of experimental dependences of $\ln k$ on P is used to determine the continuous dependence of the activation volume $\Delta V^{\#}$ on P in the solvents cyclohexane, anisole, toluene, n-nonane, isopropylbenzene, and *tert*-butylbenzene. The dependences of $\Delta V_s^{\#}$, $\Delta V_d^{\#}$, $V_r^{\#}$ on P are synchronous and nonordinary, and their nature significantly depends on the choice of a solvent. Spline approximation of experimental dependences of the TMSCP concentrations on the reaction time in isopropylbenzene at various P is used to find differential constants k_s, which generally increase with the reaction time, especially in the pressure interval 5–10 kbar.

It is known [1–6] that trimethylsilyl(cumyl) peroxide (TMSCP) forms the products of its rearrangement and decomposition upon heating at atmospheric and higher pressures. The rate of conversion can be described by the integral first-order rate law. When determining the activation volume, the equation from the theory of activated complex is used.

$$(\mathrm{d}\ln k/\mathrm{d}P)_T = -\Delta V^{\#}/RT. \tag{1}$$

Usually, empirical equations that relate $\ln k$ and P are used in the calculations, and the differentiation of these equations makes it possible to find $\Delta V^{\#}$ at different P. These equations usually reflect the fact that the absolute value of the activation volume decreases with an increase in P; this is supported by numerous experimental data [7]. However, results reported in [2, 4–6] describe the dependence of $\ln k$ on P for the thermal decomposition of TMSCP and suggest more complex changes in $\Delta V^{\#}$ with an increase in P. Therefore, the method for calculating $\Delta V^{\#}$ described above is not applicable. In this study, we used the method of spline approximation (SA) with the SPLINE REGS algorithm [8]. The essence of experimental data processing by this method generally consists in the piecewise-polynomial approximation by the curves $f(x)$ consisting of pieces of cubic polynomials and providing the minimum of the functional $\delta S(f) + (1 - \delta)C(f)$, where $S(f)$ is the sum of squared deviations of the values of func-

tion $f(x)$ from the experimental values and $C(f)$ is the integral of the square of the second derivative $\mathrm{d}^2 f(x)/\mathrm{d}x^2$. Paramter δ (it was denoted in [8] as PP) is introduced by a user of the algorithm and ranges from 0 to 1. The higher the value of δ, the better is the fit of the curve to experimental points, but the curve is smooth anyway. As a result the algorithm with given δ creates a continuous curve through, for instance, the experimental points of the $\ln k$–P dependence and simultaneously gives the continuous derivative of this curve, which is equal to $-\Delta V^{\#}/RT$.

According to the experiment, the value of the overall rate constant k_s determined from the TMSCP consumption in time is equal to $k_r + k_d$, where k_r is the rate constant of rearrangement, and k_d is the rate constant of radical decomposition. Therefore, the ratio of the amounts of products of rearrangement and radical decomposition is equal to k_r/k_d. All the three rate constants are determined from these ratios, and the SA method is used to determine the dependence of $\ln k$ on P and $-\Delta V^{\#}$ on P with Eq. (1). Note that in calculating k_r/k_d, the values of fractions of products of rearrangement and radical decomposition were preliminarily smoothened by spline with $\delta = 0.05$ with respect to pressure. The rate constants and their ratios are shown in Table 1.

Figures 1–3 show the dependences of $-\Delta V^{\#}$ on $-P$ for six solvents. As can be seen, in none of the solvents except for cyclohexane, the reaction does not occur in such a manner that the accelerating effect of pressure

† Deceased.

Table 1. The values of the overall rate constants ($k_s \times 10^5$, s^{-1}) and the ratios of the rate constants of rearrangement (k_r) and radical decomposition (k_d) of TMSCP in various solvents ($C_0 = 0.2$ M) at various pressures and ($T = 443$ K) obtained in experiments and calculated by the method of spline approximation

P, kbar	Experiment*		Calculation		Experiment*		Calculation	
	k_r/k_d	k_s	k_r/k_d***	k_s**	k_r/k_d	k_s	k_r/k_d***	k_s**
	t-Butylbenzene				Isopropylbenzene			
0.2	0.79	1.3	0.96	1.18	1.15	1.15	1.15	1.17
0.5	0.79	1.25	0.99	1.20	–	–	1.15	1.25
1.0	1.08	1.2	1.04	1.25	1.26	1.5	1.11	1.38
2.0	1.66	1.25	1.15	1.40	0.98	1.85	1.06	1.66
2.5	–	–	1.16	1.51	0.84	1.75	1.04	1.80
4.0	1.60	2.2	1.29	2.15	1.12	2.3	0.99	2.22
5.0	1.21	3.4	1.32	2.74	0.94	2.6	0.96	2.57
7.5	1.10	3.9	1.25	3.96	1.0	3.7	0.84	3.79
10	1.11	4.6	1.14	4.70	0.63	6.0	0.70	5.90
	n-Nonan				Toluene			
0.2	0.61	1.8	0.71	1.77	1.15	1.6	1.17	1.57
1.0	0.85	1.9	0.66	1.92	1.02	1.6	1.18	1.67
2.5	0.55	2.2	0.57	2.23	1.18	2.0	1.20	1.88
4.0	–	–	0.49	2.64	1.49	2.1	1.19	2.13
5.0	0.38	3.2	0.45	2.97	1.22	2.3	1.15	2.36
7.5	0.37	3.7	0.37	4.20	–	3.4	0.94	3.53
9	–	–	0.34	5.74	0.77	–	0.81	4.91
10	0.34	8.2	0.32	7.69	0.67	6.5	0.72	6.28
	Cyclohexen				Anisole			
0.2	1.20	3.2	1.14	3.4	0.45	3.5	0.40	3.6
0.8	1.12	4.0	1.12	4.33	–	–	0.39	3.9
1.0	1.05	4.6	1.11	4.7	0.35	4.5	0.39	4.1
1.5	1.02	7.0	1.10	5.7	–	–	0.39	4.38
2.5	1.18	7.9	1.08	8.2	0.41	4.5	0.38	5.1
4.0	1.10	–	1.04	13	–	–	0.37	6.8
5.0	0.96	17.1	1.01	17	0.32	9.0	0.37	8.2
7.5	0.89	31	0.95	31.2	0.41	11.3	0.39	11.6
10	0.95	53.5	0.91	54	0.43	16.0	0.42	16.0

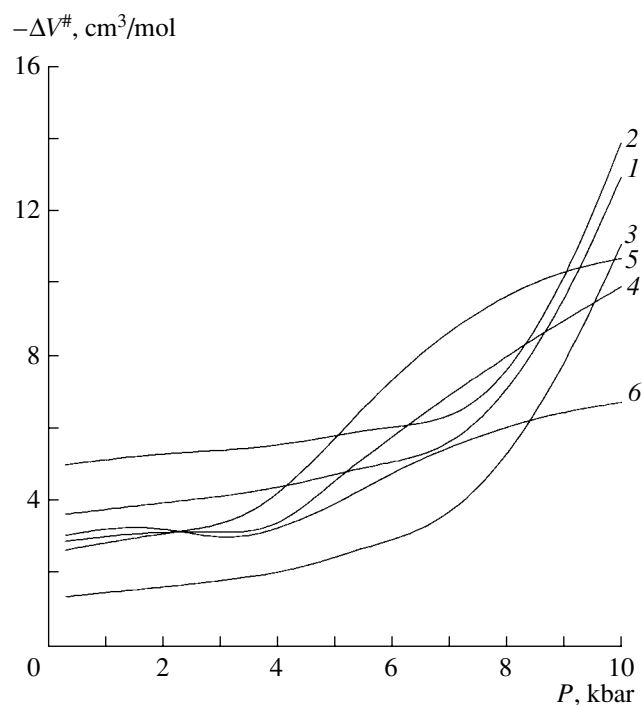 * [2, 4–6].
 ** The values of k_s correspond to those obtained by spline aproximation of the experimental curve ln$k$–P with $\delta = 0.28$.
 *** Smoothened values (see text).

$-\Delta V^{\#}$, cm^3/mol
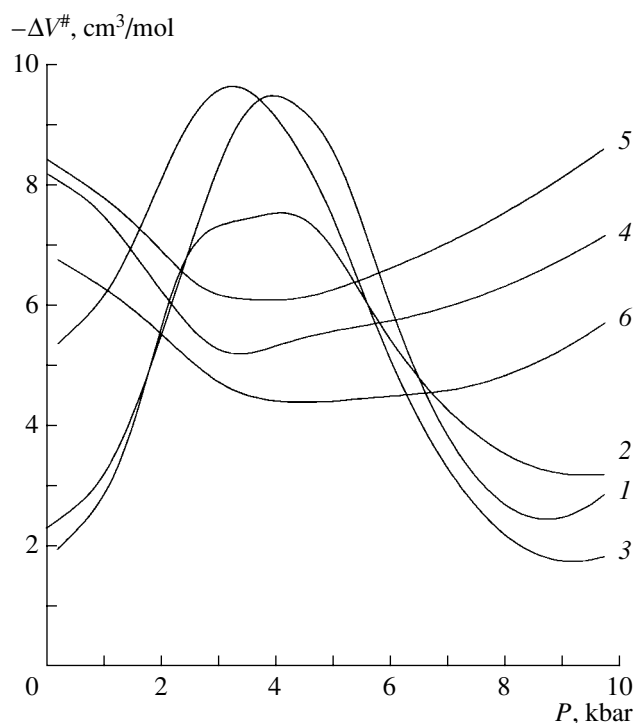
Fig. 1. Dependence of the activation volumes of the reaction of TMSCP on pressure in the solvents (*1, 2, 3*) *t*-butylbenzene and (*4, 5, 6*) isopropylbenzene. (*1, 4*) $\Delta V_s^{\#}$; (*2, 5*) $\Delta V_d^{\#}$; and (*3, 6*) $\Delta V_r^{\#}$.

$-\Delta V^{\#}$, cm^3/mol

Fig. 2. Dependence of the activation volumes of the reaction of TMSCP on pressure in the solvents (*1, 2, 3*) *n*-nonane and (*4, 5, 6*) toluene. (*1, 4*) $\Delta V_s^{\#}$; (*2, 5*) $\Delta V_d^{\#}$; and (*3, 6*) $\Delta V_r^{\#}$.

diminished in the whole pressure range. On the other hand, this effect increased in *n*-nonane and toluene (Fig. 2).

There are many papers where the value and sign of the activation volume $\Delta V_0^{\#}$ at an atmospheric pressure are used to judge the structure of the activated complex in a reaction. Specifically, in the rearrangements of organosilicon peroxides without radical decomposition, the cyclic intramolecular activated complex was assumed [1]. Such reactions have been studied at high pressures [9, 10]. The value of $-\Delta V_0^{\#}$ found in these papers is within 7–10 cm^3/mol in anisole as a solvent. These values were calculated by the usual methods, and the value of the activation volume was assigned to a change in the volume in the formation of the cyclic intramolecular activation complex. Because in the thermal transformations of TMSCP in anisole the ratio of rearrangement and thermal decomposition products does not change with a change in the pressure, it was concluded that the activated complex is the same when the products of these two processes are formed. The synchronous nature of the dependences in Figs. 1–3 in different solvents supports this conclusion. However, the values of $-\Delta V_0^{\#}$ differ substantially.

Let us consider these values using the example of the $-\Delta V_s^{\#}$ values, which are more accurate. These are (in cm^3/mol) 2.3 for *t*-butylbenzene, 8.2 for isopropylbenzene, 3.6 for *n*-nonane, 2.8 for toluene, 16 for cyclohexene, and 5.8 for anisole.

Comparison of these values with the reactivity at the initial pressure (0.2 kbar) does not reveal any relationship (see Table 1). This is confirmed by data from the study of the pressure effect on the rates of transformation of trimethylsilyl(trityl) peroxide in anisole (443 K, $k_s \times 10^5 = 13.9$ s^{-1}; 0.2 kbar) [4] and cyclohexane (433 K, $k_s \times 10^5 = 8.4$ s^{-1}; 0.2 kbar) [6]. These rate constants are 4–5 times higher than the corresponding values for TMSCP, the values of $-\Delta V_0^{\#}$ are two times lower, and the activation volumes change in a different manner with an increase in *P* (Fig. 4).

A question arises of whether the rate constants vary in the course of the process. To address this question we also used the SA method, which makes it possible to determine the differential rate constants $k_t = -dC/Cdt$ from the dependences of *C* on *t*, where *C* is the concentration of TMSCP at time *t*.

Unfortunately, data sufficient for spline approximation are only available for isopropylbenzene [2]. Approximation was carried out with δ = 0.05 and the
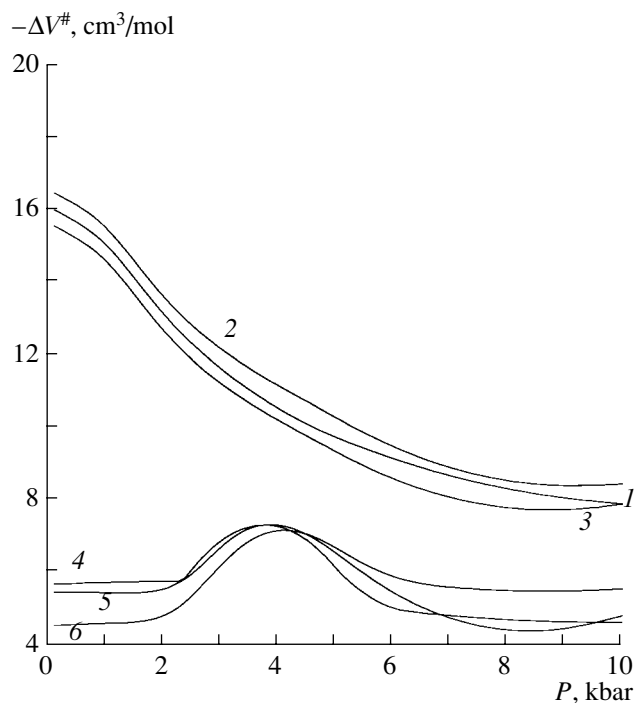
Fig. 3. Dependence of the activation volumes of the reaction of TMSCP on pressure in the solvents (*1, 2, 3*) cyclohexene and (*4, 5, 6*) anisole. (*1, 4*) $\Delta V_s^{\#}$; (*2, 5*) $\Delta V_d^{\#}$; and (*3, 6*) $\Delta V_r^{\#}$.
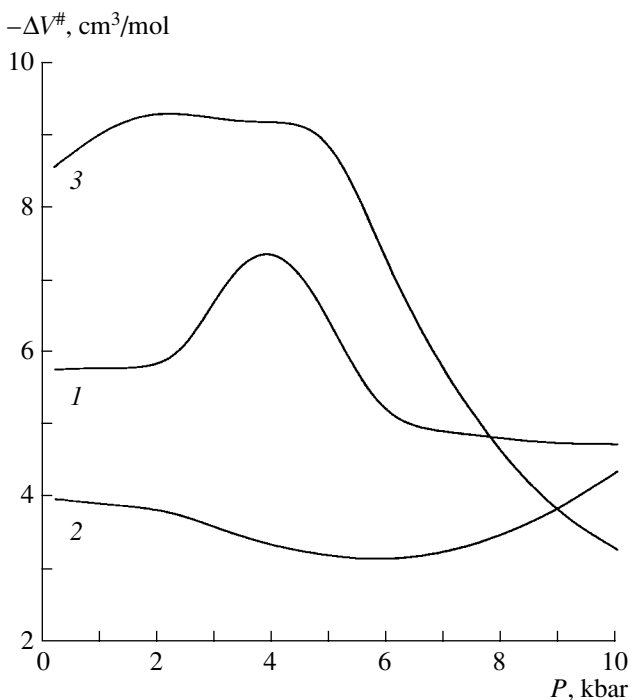
Fig. 4. Dependence of the activation volumes $(-\Delta V_s^{\#})$ on the pressure. (*1*) TMSCP in anisole and trimethylsilyl(trityl) peroxide in (*2*) anisole and (*3*) cycohexene.
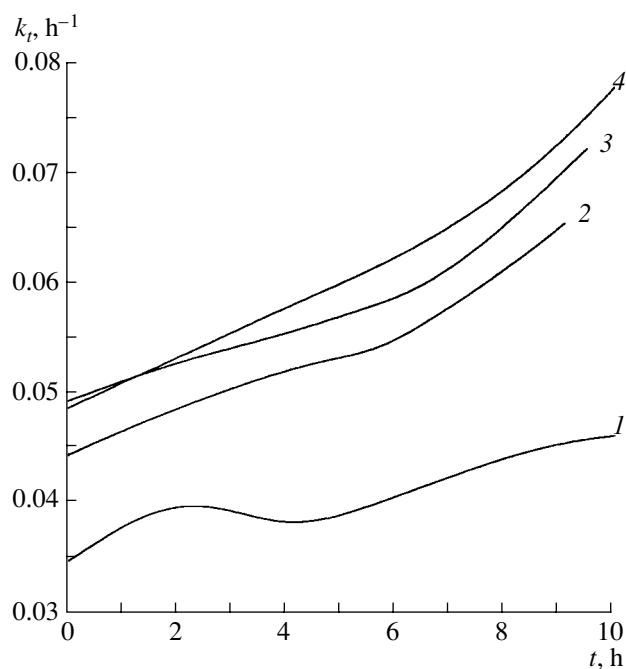
Fig. 5. Dependence of the differential overall rate constant of the reaction of TMSCP on the reaction time in isopropylbenzene. (*1*) 0.2, (*2*) 0.5, (*3*) 1, and (*4*) 2.5 kbar.
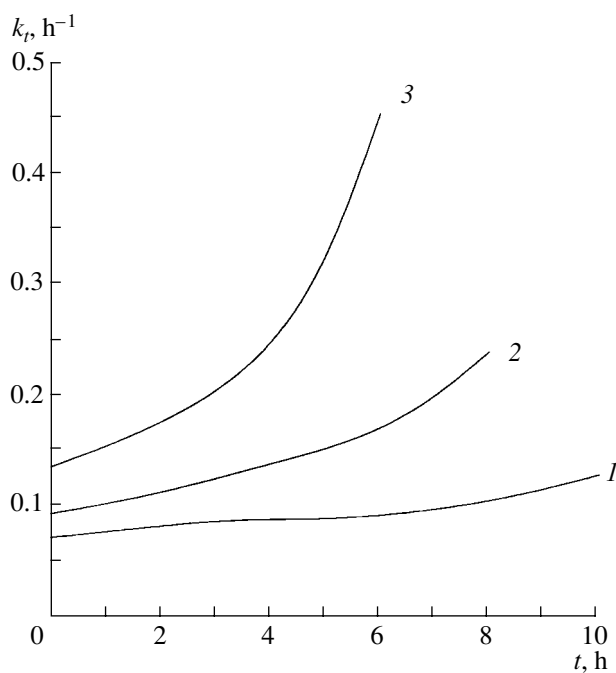
Fig. 6. Dependence of the differential overall rate constant of the reaction of TMSCP on the reaction time in isopropylbenzene. (*1*) 5, (*2*) 7.5, and (*3*) 10 kbar.

Table 2. Spline approximation of the experimental dependence of the TMSCP concentration on time at various pressures and $T = 443$ K

P, kbar	t, h	[TMSCP], mol/l		P, kbar	t, h	[TMSCP], mol/l	
		experiment	calculation			experiment	calculation
0.2	0	0.190	0.188	5.0	0	0.189	0.186
	3	0.166	0.167		2	0.161	0.160
	3.5	0.159	0.164		3.25	0.144	0.143
	5	0.159	0.155		3.67	0.137	0.138
	5.5	0.153	0.152		4	0.129	0.134
	6.08	0.147	0.148		5	0.122	0.123
	7.5	0.145	0.140		9.83	0.076	0.075
	8	0.130	0.137		10	0.074	0.073
	10	0.126	0.125	7.5	0	0.178	0.174
0.5	0	0.189	0.188		1	0.155	0.158
	3.5	0.159	0.159		3	0.132	0.126
	5	0.144	0.147		4	0.106	0.110
	8	0.126	0.124		5	0.088	0.095
	9.08	0.115	0.116		7	0.067	0.068
1.0	0	0.189	0.186		8	0.060	0.054
	1.5	0.171	0.173	10	0	0.178	0.166
	2.5	0.163	0.164		1	0.137	0.144
	3.5	0.155	0.155		2	0.116	0.122
	5	0.142	0.143		3	0.099	0.101
	6	0.132	0.135		5	0.060	0.061
	7.5	0.126	0.123		6	0.047	0.042
	8	0.119	0.119				
	9	0.110	0.111				
	9.5	0.108	0.107				
2.5	0	0.188	0.187				
	3	0.160	0.160				
	5	0.141	0.142				
	7	0.125	0.126				
	9	0.109	0.109				
	10	0.103	0.102				

results are shown in Table 2 and in Figs. 5 and 6. It can be seen from these figures that the values of k_t increase with an increase in t in all cases. Generally, the higher the value of P, the more pronounced is an increase in k_t. One might expect a change in the nature of the dependence of $\Delta V^{\#}$ on P, if the value of k_t at $t = 0$ were used. Figure 7 shows the corresponding results of the calculation (curve *2*). For comparison, the same figure shows the results of calculation with constants obtained from the first-order rate law (curve *1*). Because, according to our data, the reaction rate $-(dC/dt)$ changes insignificantly with the reaction time, unlike the value dC/Cdt, and is practically independent of the pressure, the average values of $-dC/dt$ were calculated for each pressure, and the dependence $\Delta V^{\#}$ on P (Fig. 7, curve *3*) was obtained by SA of the dependence of $\ln(-dC/dt)$ on P. As can be seen from Fig. 7, the nature of the curves is almost the same but both the initial and average values of $-\Delta V^{\#}$ differ substantially; they decrease from curve *1* to curve *3*. The weakness of the dependence of $-dC/dt$ on t means that the reaction order is lower than unity at all pressures. Therefore, curve *3* more accurately describes the dependence of $\ln k$ on P, but the minimum is observed at the same pressure for all curves. That is, the curves do not correspond to the usual change in the activation volume with an increase in the pressure. The reaction order is most likely to decrease with an increase in the pressure. Thus, at $P = 0.2$ kbar for 10 h, the reaction rate decreases by 13% and the concentration increases by 34%. At $P = 10$ kbar for 6 h, the reaction rate decreased almost to the same degree (by 15%), and the concentration decreased by 75%.

The fact that the apparent reaction order is not first can be explained by the existence of energy chains, the role of which changes depending on pressure, the reaction rate (and, therefore, the initial concentration), and the nature of the solvent. For example, see data on the reaction of TMSCP in anisole at a four times lower concentration (0.05 M) [4]. Calculation using these data showed that $-\Delta V^{\#} = 2$ cm³/mol in the pressure interval up to 5 kbar and increases to 8 cm³/mol in the next interval up to 10 kbar. Thus, the anomalous increase in $-\Delta V^{\#}$ in this case shifts toward the region of higher pressures. Moreover, these data show that the value $-\Delta V_0^{\#}$ in anisole should be ~2 cm³/mol rather than 5.8 as mentioned above. In general, taking into account the results obtained, probably except for the results for cyclohexane, we conclude that a change in the volume in the formation of the activated complex in the reactions of TMSCP in various solvents is at most 3 cm³/mol. The apparent values that are much higher
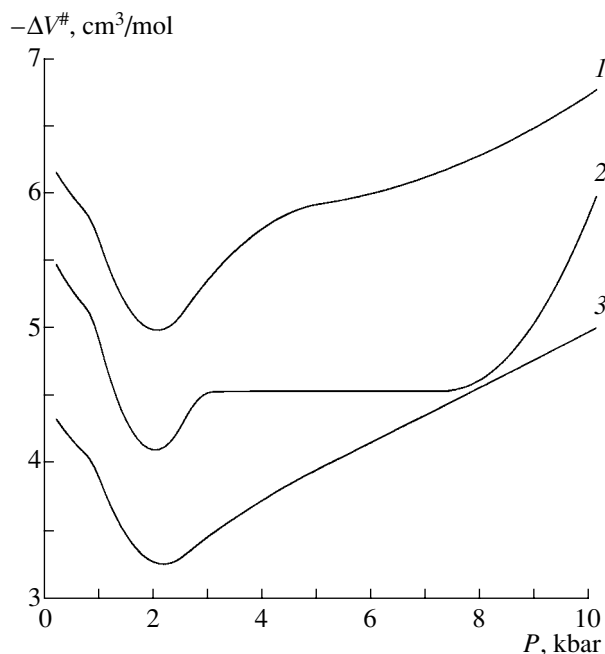

Fig. 7. Dependence of the activation volumes $(-\Delta V_s^{\#})$ on the reaction pressure for the reaction of TMSCP in isopropylbenzene (see text).

are due to other factors, specifically, the existence of energy chains as presumed in this work.

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