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Effect of High Pressure on the Kinetics and Mechanism of Thermolysis of Organic Peroxides in Solution

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Abstract—This review analyzes published data and experimental results obtained by the authors concerning the effect of high pressure on the chemical kinetics of thermal decomposition of the main types of organic and organosilicon peroxides in solution. The volume effect of activation was found to depend on the mechanism of peroxide decomposition and on the properties of solvents.

High reactivities and various structures of organic peroxides are responsible for their wide use in chemistry and chemical technology [1–4].

Pressure is one of the most important factors affecting the rates and directions of chemical reactions. Knowledge of reaction volume characteristics, which are derived from the pressure dependence of the reaction rate, provides an opportunity to refine the structure of the transition state and the reaction mechanism. A study of the effect of high pressure on the thermal transformations of peroxide compounds (dialkyl peroxides, peroxycarbonates, etc.) is of particular practical interest because they are commonly used as initiators for the radical polymerization of ethylene [5–11]. This high-pressure polymerization is commercially implemented on a large scale. Polyethylene and its copolymers are produced with the use of radical initiators at pressures of 150–300 MPa and temperatures of up to 280°C. The manufacturing unit capacity of high-pressure polyethylene production is as high as hundred thousands of tons per annum.

Depending on the thermal stability of the peroxide in use and on the reactivity of the resulting radical products of thermolysis, the process parameters of polymerization and the quality of the resulting polymer are changed. As the temperature is increased, the rate of ethylene conversion increases; this increase is accompanied by a decrease in the average molecular weight of polyethylene, an increase in its branching, and an increase in the double bond content. An increase in the pressure increases the rate of the process, the molecular weight, and the density of the product.

The effect of pressure on the rate constant of a chemical reaction at a constant temperature is described by the equation

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\neq}}{RT}, \qquad (1)$$

where $\Delta V^{\neq}$ is the volume effect of activation—the change in the volume on the formation of 1 mol of an activated complex.

General principles used in studies of the effect of pressure on chemical reactions, including homolytic transformations, were considered in [12–17]. The value of $\Delta V^{\neq}$ determined at atmospheric pressure is designated $\Delta V_0^{\neq}$. The sign of $\Delta V_0^{\neq}$ indicates the sense of changing the reaction rate constant with pressure. The value of $\Delta V_0^{\neq}$ at a given P is determined from the slope of a curve plotted for the logarithm of the reaction rate constant as a function of pressure. Some authors calculated $\Delta V_0^{\neq}$ from the slope of a straight line drawn through the initial points of the experimental $\ln k_P$–P relationship, where k_P is the reaction rate constant at pressure P.

A number of functions were proposed for the determination of $\Delta V_0^{\neq}$ from experimental data; these functions were considered by El'yanov and Vasylvitskaya [14]. El'yanov and coauthors [14, 17] recommended the following linear free-energy relationship for nonionic, in particular, homolytic, reactions:

$$\log\frac{k_P}{k_0} = -\frac{\Delta V^{\neq}\Phi}{T}, \qquad (2)$$

where the subscripts P and 0 refer to pressure P and atmospheric pressure, respectively, and Φ is a function of pressure; these functions are identical for related reactions and different for reactions of different types. For nonionic liquid-phase reactions,

$$\Phi = \left[(1+\alpha)P - \frac{\alpha}{\beta}(1+\beta P)\right]/R\ln 10, \qquad (3)$$

where α can be taken as equal to 0.170 and β is approximately equal to 4.94×10^{-8} Pa^{-1}. These coefficients

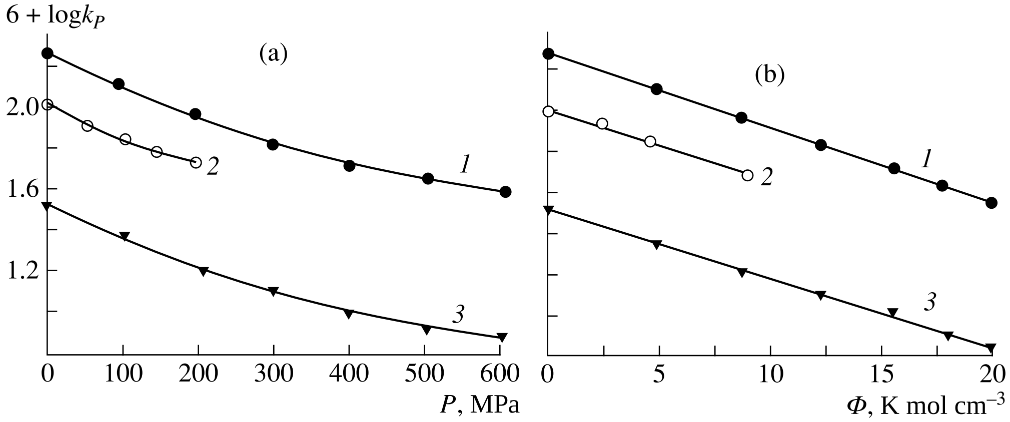


Fig. 1. logk_P as a function of (a) pressure or (b) parameter Φ in the decomposition of dicyclohexylperoxydicarbonate in (*1*) acetonitrile, (*2*) benzene, or (*3*) toluene. C_0 = 0.2 mol/l; T = 323 K.

were obtained from accurate data for a Diels–Alder reaction.

Data optimization for many reactions resulted in different values of α and β. However, the values of Φ calculated with the use of both pairs of the coefficients differ only within 2 or 3% at pressures up to 400 MPa.

Figure 1 demonstrates the dependence of logk_P on pressure and the parameter Φ for the decomposition of dicyclohexylperoxydicarbonate [18] ($\Delta V^{\neq}$ = 10 ± 0.5 cm^3/mol).

Note that, although the values of $\Delta V^{\neq}$ are of the same order, all of the $\Delta V^{\neq}$ values obtained by different procedures used for experimental data processing are significantly different (see Table 1 for some compounds). Equation (2) makes it possible to determine $\Delta V_0^{\neq}$ from only two rate constants measured at two pressures. For complex processes including a number of elementary steps, $\Delta V^{\neq}$ of the overall process is the sum of the activation volumes of elementary steps. In this case, only the ratio between rate constants and the total activation volume can be determined.

Problems associated with the interactions of reactants with each other and of the transition state with the solvent, as well as with the cage effect in homolytic reactions, occur in studies of the effect of pressure on reactions in solutions. Because the initial reactants and the transition state interact with the solvent, the experimentally determined effective activation volume $\Delta V_0^{\neq}$ is the sum of structural changes on the formation of the transition state and the solvation volume $\Delta V_{\text{sol}}^{\neq}$, which is the sum of volume changes of reactants, the transition state, and their solvate shells under the action of the solvent. In the simplest cases when these changes are determined by only the dipole–dipole interaction, the Kirkwood equation can be used. However, in reality, the interaction of the solvent and reactants is not restricted by only electrostatic forces.

The viscosity of liquids significantly increases with pressure; consequently, translational and rotational movements of reacting particles are slowed down. In thermal reactions accompanied by the homolysis of bonds, the reactions of resulting radicals in solvent cages are of considerable importance. Evidently, the viscosity changed under the action of pressure affects the rates and ratios between these reactions. As a result, the experimentally determined volume effect of activation is changed.

The viscosity dependence of the rate constant of decomposition k_d of an initiator is observed when only one bond is cleaved, because with the simultaneous cleavage of two bonds radicals are formed at a distance, which excludes their recombination in a cage. Accord-

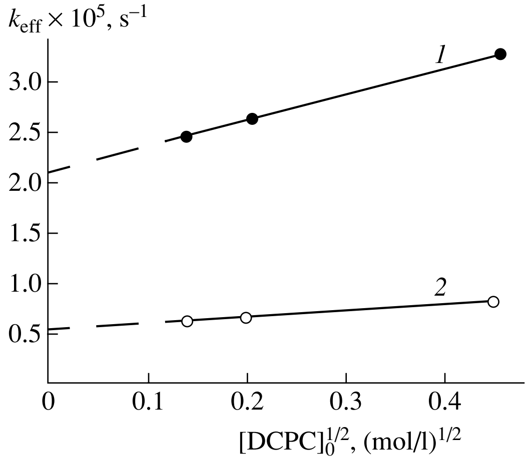


Fig. 2. Concentration dependence of the effective rate constant of dicyclohexylperoxydicarbonate (DCPC) decomposition ($k_{\text{eff}} = k_1 + k_{\text{ch}}[\text{DCPC}]^{1/2}$) in toluene at a pressure of (*1*) 0.1 or (*2*) 500 MPa; T = 323 K.

Table 1. Volume effects of activation in the thermolysis of azo compounds

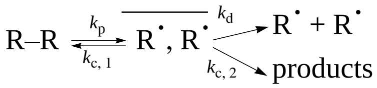
Compound	Solvent	T, K	P, MPa	$\Delta V^{\neq}$, cm^3/mol			Reference
				published data	calculated by Eq. (2)	calculated by Eq. (1)	
Di-*tert*-butyl hyponitrite	*n*-octane	328	0.1–620	4.4	7.1	4.3	[19]
Azocumeme	cumene	328	0.1–610	5.3	8.5	5.0	[20]
	chlorobenzene	328	0.1–610	4.7	6.5	4.3	[20]
(Phenylazo)triphenylmethane	*n*-octane	323	0.1–421	16.9	25.5	16.4	[21]
	cumene	323	9.1–421	20.2	29.2	18.8	[21]

ing to Le Noble [22], the true volume effects of activation $\Delta V_{\rm t}^{\neq}$ for various reactions are the following:

Reaction type	$\Delta V_{\rm t}^{\neq}$, cm^3/mol
Bond cleavage	+10
Bond deformation	~0
Bond formation	–10
Substitution	–5
Diffusion-controlled	+20
Cyclization	0
Sterically hindered	(–)
Ionization	–20

In the homolytic cleavage of a bond in peroxides or azo compounds, $\Delta V_{\rm t}^{\neq} \approx 10$ cm^3/mol, whereas $\Delta V_{\rm t}^{\neq} \approx$ 3–5 cm^3/mol on the concerted cleavage of two bonds, which occurs with the formation of a compact transition state.

Table 2 summarizes actual values of $\Delta V^{\neq}$ for peroxide thermolysis reactions, which vary from 0 to 20 cm^3/mol. The simple scheme of the cage effect



suggests that

$$k_{\rm eff} = k_{\rm p}(k_{\rm d}/(k_{\rm c} + k_{\rm d}) = k_{\rm p}e,$$

where e is the fraction of radicals escaped from cages into the bulk, $k_{\rm c}$ is the rate constant of overall cage recombination reactions to form initial molecules and other molecular products of radical reactions, and $k_{\rm d}$ is the rate constant of radical diffusion from a cage to the bulk.

According to Zhulin [16], $(1 - e)/e = k_{\rm c}/k_{\rm d}$; then,

$$\left(-RT\left(\partial\ln\frac{1-e}{e}\right)/\partial P\right)_T = \Delta V_{\rm c}^{\neq} - \Delta V_{\rm d}^{\neq},$$

where $\Delta V_{\rm c}^{\neq}$ and $\Delta V_{\rm d}^{\neq}$ are the volume effects of activation of cage radical reactions and radical escape from the cage, respectively. Equating $\Delta V_{\rm d}^{\neq}$ to the volume effect of viscous flow, we obtain

$$\left(\frac{\partial\ln V\eta}{\partial P}\right)_T = \frac{\Delta V_{\rm d}^{\neq}}{RT}, \qquad (4)$$

where V and η are the molar volume and the solvent viscosity, respectively. Because the molar volume decreases with pressure to a much lesser extent than the viscosity increases, $\Delta V_{\rm d}^{\neq}$ is positive; this reflects the necessity of repulsing other molecules on the migration of a given molecule. For many solvents, this value lies within the range 10–20 cm^3/mol; for example, $\Delta V_{\rm d}^{\neq}$ = 15 cm^3/mol for toluene. This results in a considerable difference between experimental $\Delta V^{\neq}$ and the $\Delta V^{\neq}$ characteristic of the reaction itself.

Based on the measurements of the volume effects of activation for the translational ($\Delta V_{\rm tr}^{\neq}$) and rotational ($\Delta V_{\rm r}^{\neq}$) movements of molecules in solution [47–49] (Table 3), Zhulin [13–15] substantiated this interpretation of the effect of pressure on $k_{\rm c}$ and $k_{\rm d}$. Jonas [49] found that $\Delta V_{\rm tr}^{\neq}$ is almost equal to the value of $\Delta V_{\rm d}^{\neq}$ found from Eq. (4), and $\Delta V_{\rm r}^{\neq} \ll \Delta V_{\rm tr}^{\neq}$.

Replacing $\Delta V_{\rm c}^{\neq} - \Delta V_{\rm d}^{\neq} = \Delta V_{\rm r}^{\neq} - \Delta V_{\rm tr}^{\neq}$, we find that $\Delta V_{\rm c}^{\neq} - \Delta V_{\rm d}^{\neq}$ in ordinary solvents can vary from –15 to 0 cm^3/mol. That is, both systems in which the cage effect weakly depends on pressure ($\Delta V_{\rm c}^{\neq} \approx \Delta V_{\rm d}^{\neq}$) and systems (for example, in benzene) in which $k_{\rm c}/k_{\rm d}$ increases with pressure (that is, an increase in the pressure slows down cage radical reactions more weakly than radical escape from the cage) can occur. The work of Jonas [49] also suggests that molecular geometry is

Table 2. Volume effects of activation in the thermolysis of peroxides in solution

Peroxide and the main reaction of thermolysis	Solvent	T, °C	P, MPa	$\Delta V^{\neq}$, cm^3/mol	Reference
Alkyl peroxides					
$Me_3COOCMe_3 \longrightarrow 2Me_3CO^{\bullet}$	2-isopropyl-1,3-dioxolane	130	980	11	[23]
	2-(cyclohexyl)tetrahydropyrane	130	500	21	[24]
	heptane	140	230	10.5	[25]
	heptane	160	230	7.9	[25]
	heptane	180	230	11.6	[25]
	heptane	190	230	8.6	[25]
	heptane	200	230	10.1	[25]
	isodecane	143–230	300	13.4	[6]
	PhH	120	714	12.6	[26]
	PhMe	120	527	5.4	[26]
	CCl_4	120	563	13.3	[26]
	cyclohexane	120	584	6.7	[26]
$PhCMe_2OOCMe_2Ph \longrightarrow 2PhCMe_2O^{\bullet}$	$PhCH_3$	126	700	14.77	[27]
	$PhCD_3$	126	700	20.6	[27]
	$C_6D_5CD_3$	126	700	24.0	[27]
	iso-PrPh	126	400	19.6	[27]
	tert-BuPh	126	600	22.3	[27]
	PhH	126	800	7.4	[27]
3,3,4,4-Tetramethyl-1,2-dioxetane $\longrightarrow 2Me_2CO$	PhMe	60	100	9	[28]
	PhCl	60	100	11	[28]
$Me(Et)C(OOCMe_3)_2$	isodecane	200	200	22.3	[11]
Diacyl peroxides					
$Me_2CHC(O)OOC(O)CHMe_2 \longrightarrow 2Me_2CHC(O)O^{\bullet}$	isooctane	50	300	–5.1	[29]
$[n\text{-}C_7H_{15}C(O)O–]_2$	isooctane	80–200	300	5.9	[6]
$[MeOC(O)(CH_2)_3C(O)O–]_2 \longrightarrow 2MeOC(O)(CH_2)_3^{\bullet} + 2CO_2$	PhMe	70	980	1.6	[30]
$PhC(O)OOC(O)Me \longrightarrow PhC(O)O^{\bullet} + {}^{\bullet}OC(O)Me$	PhCl	96	190	4	[31]
$PhC(O)OOC(O)Ph \longrightarrow 2PhC(O)O^{\bullet}$	CCl_4	60	200	8.7	[32]
	CCl_4	70	300	8.7	[32]
	acetophenone	80	150	4.8	[33]
	allyl acetate	80	550	4.7	[33]
$[cyclo\text{-}C_6H_{11}OC(O)O–]_2 \longrightarrow 2cyclo\text{-}C_6H_{11}OC(O)O^{\bullet}$	MeCN	50	500	10.1	[18]
	PhMe	50	500	11.9	[18]
	PhH	50	200	7.9	[18]
	cyclohexanol	50	200	13.7	[18]
	cyclohexanone	50	200	15.8	[18]
	isodecane	107	300	43	[6]
$\xrightarrow{+2HR} 2Me_3CCH_2CHMe_2 + 2CO_2 + 2R^{\bullet}$	n-heptane	80	250	2.9	[34]
$[Me_3CCH_2CH(Me)CH_2C(O)O–]_2$	n-pentadecane	80	200	2.8	[34, 35]
$\longrightarrow [Me_3CCH_2CH(Me)CH_2–]_2 + 2CO_2$	PhMe	80	300	2.0	[35]

Table 2. (Contd.)

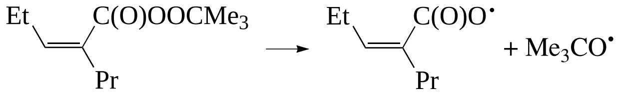
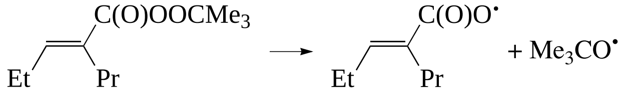
Peroxide and the main reaction of thermolysis	Solvent	T, °C	P, MPa	$\Delta V^{\neq}$, cm^3/mol	Reference
	$C_2H_4Cl_2$	70	300	3.0	[35]
	MeCN	70	300	0.88	[35]
Peroxyesters					
$Me_2CHC(O)OOCMe_3 \longrightarrow Me_2CH^{\bullet} + CO_2 + Me_3CO^{\bullet}$	*iso*-PrPh	65	510	1.6	[36]
$Me_3CC(O)OOCMe_3 \longrightarrow Me_3C^{\bullet} + CO_2 + Me_3CO^{\bullet}$	*tert*-BuPh	65	500	0.3	[36]
	heptane	70	200	1.7	[37]
	heptane	80	200	2.8	[37]
	heptane	90	200	3.4	[37]
	heptane	105	200	1.2	[37]
	isodecane	80	300	5.9	[38]
	″	120	300	4.2	[38]
	″	140	300	6.2	[38]
	″	200	300	4.4	[38]
	″	80–200	300	6.1	[6]
	″	120–200	300	9.4	[6]
$Me_3CC(O)OOCMe_2Et \longrightarrow Me_3C^{\bullet} + CO_2 + EtMe_2CO^{\bullet}$	″	120	300	9.2	[38]
	″	150	300	15.2	[38]
	″	200	300	11.6	[38]
$Me_3CC(O)OOC(Me)(Pr)Bu \longrightarrow Me_3C^{\bullet} + CO_2 + Bu(Pr)(Me)CO^{\bullet}$	″	120	300	10.1	[38]
	″	140	300	14.6	[38]
	″	180	300	6.2	[38]
	″	200	300	7.0	[38]
$Me_3CC(O)OOCMe_2CH_2CH_2CHMe_2$	″	120	300	10.7	[38]
$\longrightarrow Me_3C^{\bullet} + CO_2 + Me_2CHCH_2CH_2Me_2CO$	″	140	300	9.2	[38]
	″	200	300	8.6	[38]
$Me_3C(CH_2)_5C(O)OOCMe_3$	″	100–200	300	6.1	[6]
$Me_3C(CH_2)_5C(O)OOCMe_2Et$	″	100–200	300	7.0	[6]
$Me(CH_2)_4(Me)(Et)CC(O)OOCMe_3$	″	100	300	5.3	[38]
$\longrightarrow Me_3CO^{\bullet} + CO_2 + Me(CH_2)_4(Me)(Et)C^{\bullet}$	″	130	300	7.1	[38]
	″	200	300	6.4	[38]
$Me(CH_2)_4(Me)(Et)CC(O)OOCMe_2Et$	″	100	300	6.3	[38]
$\longrightarrow EtMe_2CO^{\bullet} + CO_2 + Me(CH_2)_4(Me)(Et)C^{\bullet}$	″	130	300	7.5	[38]
	″	200	300	6.7	[38]
$Me(CH_2)_4(Me)(Et)CC(O)OOCMe_2CH_2CH_2CHMe_2$	″	100	300	9.3	[38]
$\longrightarrow Me_2CHCH_2CH_2Me_2CO^{\bullet} + CO_2 + Me(CH_2)_4(Me)(Et)C^{\bullet}$	″	120	300	13.0	[38]
	″	200	300	5.5	[38]
	*iso*-PrPh	100.1	400	6.8	[19]

Table 2. (Contd.)

Peroxide and the main reaction of thermolysis	Solvent	T, °C	P, MPa	$\Delta V^{\neq}$, cm^3/mol	Reference
	*iso*-PrPh	100.1	400	9.0	[19]
cyclo-$C_6H_{11}C(O)OOCMe_3 \longrightarrow$ *cyclo*-$C_6H_{11}^{\bullet} + CO_2 + Me_3CO^{\bullet}$	″	79.6	410	3.9	[39]
$PhCH_2C(O)OOCMe_3 \longrightarrow PhCH_2^{\bullet} + CO_2 + Me_3CO^{\bullet}$	″	79.6	410	1.0	[40]
	″	79.6	610	0.5	[39, 40]
	″	85	410	1	[42]
	PhCl	79.6	410	1.5	[40]
	PhCl	79.6	410	1.0	[39]
$X\text{–}C_6H_4CH_2C(O)OOCMe_3 \longrightarrow X\text{–}C_6H_4CH_2^{\bullet} + CO_2 + Me_3CO^{\bullet}$					
X = *para*-Me	*iso*-PrPh	79.6	610	0.2	[41]
X = *para*-MeO	″	79.6	610	0.2	[41]
X = *meto*-Cl	″	79.6	610	1.6	[41]
X = *para*-NO_2	″	85	610	2	[42]
X = *para*-Cl	″	79.6	610	1.2	[41]
$PhC(O)OOCMe_3 \longrightarrow PhC(O)O^{\bullet} + Me_3CO^{\bullet}$	″	79.6	410	10.4	[39]
	PhCl	79.6	410	12.9	[39]
Organosilicon peroxides					
$Me_3SiOOCPh_3 \longrightarrow MeOCMe_2OCPh_3, Me_3SiO^{\bullet}, Ph_3CO^{\bullet}$	$PhOCH_3$	170	1000	–3.5	[43]
$Me_3SiOOCMe_2Ph \longrightarrow$ products	PhOMe	–	–	–	[43]
$Ph_3SiOOCMe_3 \longrightarrow$ products	″	–	–	–	[43]
$[PhCH_2Me_2SiO\text{–}]_2 \longrightarrow PhCH_2OSiMe_2OSiMe_2CH_2Ph$	″	90	980	–8	[44]
$Me_3SiOOSiMe_3 \longrightarrow MeOSiMe_2OSiMe_3$	″	135	980	–10	[45]
$[X\text{–}C_6H_4Me_2SiO\text{–}]_2 \longrightarrow X\text{–}C_6H_4OSiMe_2OSiMe_2C_6H_4\text{–}X$	″				
X = H	″	80	590	–7.9	[46]
X = *para*-MeO	″	80	590	–9.6	[46]
X = *para*-Me	″	80	590	–7.4	[46]
X = *para*-Cl	″	80	590	–8.0	[46]

more responsible for the interrelation between translational and rotational movements than dipole moment.

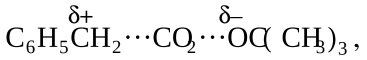
On this basis, it becomes clear why $\Delta V^{\neq}_{\text{eff}}$ in the decomposition of di-*tert*-butyl peroxide (see Table 2) varied from 5 to 13 cm^3/mol depending on the solvent. In solvents with symmetric structures, $\Delta V^{\neq}_{\text{eff}} > \Delta V^{\neq}_{P}$, whereas $\Delta V^{\neq}_{\text{eff}} \approx \Delta V^{\neq}_{P}$ in an asymmetric solvent (toluene) because $\Delta V^{\neq}_{\text{c}} \approx \Delta V^{\neq}_{\text{d}}$.

However, this approach cannot also explain all the results observed in the dependence of the kinetics of homolysis on the properties of the solvent. Thus, in the thermolysis of *para*-nitrophenylazotriphenylmethane, $\Delta V^{\neq}_{\text{eff}}$ in cumene, *n*-octane, and *tert*-butylbenzene is equal to ~20 cm^3/mol [19], although the degrees of symmetry are very different in these solvents. In this context, note that the classification of the volume effects of activation according to the number of simultaneously cleaved bonds in thermolysis is tentative.

Table 3. Volume effects of activation (cm^3/mol) for the translational ($\Delta V^{\neq}_{\mathrm{tr}}$) and rotational ($\Delta V^{\neq}_{\mathrm{r}}$) movements of molecules in solution at 23°C

Solvent	$\Delta V^{\neq}_{\mathrm{tr}}$	$\Delta V^{\neq}_{\mathrm{r}}$	$\Delta V^{\neq}_{\mathrm{r}} - \Delta V^{\neq}_{\mathrm{tr}}$
Benzene	22.0	7.4	–14.6
Acetone	13.6	4.8	–8.8
Toluene-d$_3$	14.4	10.4	–4.0
Chlorobenzene	11.2	11.7	0.5

The polar properties of a solvent for a number of peroxides can exert a crucial effect on the pressure dependence of the rate of thermolysis. Thus, in the thermolysis of *tert*-butylphenylperoxy acetate, the volume effect of activation is close to zero at pressures of 0.1–200 MPa and increases to only 3 cm^3/mol in the range 400–600 MPa [39]. Based on the polar structure of the transition state

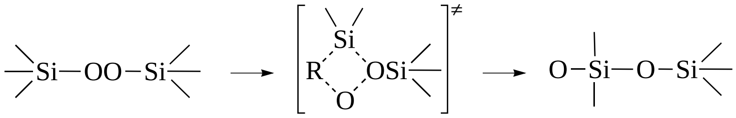


$$C_6H_5\overset{\delta+}{CH_2}\cdots CO_2\cdots\overset{\delta-}{O}C(CH_3)_3,$$

it is believed that it is solvated with solvent molecules. The solvation of the transition state increases with increasing polarity of the solvent and, at the same time, partially compensates an increase in the volume of the transition state due to the simultaneous cleavage of two bonds.

The homolytic cleavage of a typical diacyl peroxide, diisobutyryl peroxide, was accelerated with increasing pressure ($\Delta V^{\neq}_{\mathrm{eff}}$ = –5 cm^3/mol); this fact is also explained by solvation.

The thermolysis of organosilicon peroxides via a nonradical pericyclic mechanism occurs through the compact transition state, which is formed with the participation of several bonds of the parent compound,



In this case, $\Delta V^{\neq}_{\mathrm{eff}}$ is negative ($\Delta V^{\neq} = -8 \pm 2$ cm^3/mol), and the thermolysis is accelerated with pressure; this was observed for $Me_3SiOOSiMe_3$; $PhCH_2Me_2SiOOSiMe_2CH_2Ph$; and $[X–C_6H_4Me_2SiO–]_2$, where X = Cl, H, Me, or MeO (Table 2).

The asymmetric organosilicon peroxides $Me_3SiOOCMe_2Ph$, $Ph_3SiOOCMe_3$, and $Me_3SiOOCPh_3$ undergo decomposition via the following two parallel paths:

(1) with a rearrangement through a cyclic transition state with the formation of the ROSiOC≡ product;

(2) homolytically with initial O–O bond cleavage.

In these peroxides [43, 50–52], an increase in the pressure also increased the rate of thermolysis. This was observed in various solvents: *n*-nonane, toluene, cumene, *tert*-butylbenzene, cyclohexene, and anisole. In particular, in the case of trimethylsilylcumyl peroxide, the fraction of radical degradation products (dimethyl phenyl carbinol and acetophenone) remained almost unchanged with increasing pressure. However, based on a positive value of $\Delta V^{\neq}$ for homolytic O–O bond cleavage, a decrease in the yield of homolysis products with increasing pressure would be expected. Therefore, we can conclude that homolysis and decomposition with rearrangement of these peroxides occur via identical transition states.

In the thermolysis of diacyl peroxides, the contribution of chain decomposition to the overall rate of decomposition is considerable. As a rule, pressure enhances chain decomposition.

Thus, the kinetics of benzoyl peroxide (BP) decomposition on thermolysis [53] is described by the equation

$$-d[\mathrm{BP}]/dt = k_1[\mathrm{BP}] + k_{\mathrm{ch}}[\mathrm{BP}]^{3/2} = k_{\mathrm{eff}}[\mathrm{BP}],$$

where k_1 and k_{ch} are the rate constants of unimolecular and chain induced decomposition, respectively, and $k_{\mathrm{eff}} = k_1 + k_{\mathrm{ch}}[\mathrm{BP}]^{1/2}$. In this case, it was found that $\Delta V^{\neq}_1$ = 8.7 cm^3/mol and $\Delta V^{\neq}_{\mathrm{ch}}$ = –15 cm^3/mol.

The thermolysis of dicyclohexylperoxydicarbonate also occurs with a noticeable contribution of chain reactions (Fig. 2).

The values of $\Delta V^{\neq}_1$ and $\Delta V^{\neq}_{\mathrm{ch}}$ for dicyclohexylperoxydicarbonate solutions in benzene, toluene, and acetonitrile were found to be the same and equal to $\Delta V^{\neq}_1 \approx \Delta V^{\neq}_{\mathrm{ch}} \approx 11 \pm 0.5$ cm^3/mol [18, 27].

Carboxy inversion, which results in the formation of esters in the thermolysis of a number of diacyl peroxides,

$$\mathrm{RC(O)OOC(O)R'} \longrightarrow \mathrm{RC(O)OC(O){-}OR'},$$

occurs [53] with a great negative volume of activation and with lower activation energies and entropies than the simple processes of radical decomposition with the homolysis of O–O bonds.

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