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Solvent Effect on the Activation Volume of the Diels–Alder Reaction Between Tetracyanoethylene and *trans,trans*-1,4-Diphenyl-1,3-butadiene

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Abstract — The effect of increased hydrostatic pressure on the rate of the Diels–Alder reaction of tetracyanoethylene with *trans,trans*-1,4-diphenyl-1,3-butadiene at 25°C was studied to estimate the reaction volume and to show that it considerably varies with π-donor properties of the medium.

The intensive research into the effect of increased hydrostatic pressure on chemical reactions is associated both with the considerable rate and equilibrium effects of external pressure (which is especially important for practical purposes) and with a view to determination of additional activation and reaction parameters. Quantitative data on the activation volume ($\Delta V^{\neq}$) and the reaction volume (ΔV^0) of a reaction, together with its energetic characteristics, allow one to gain a deeper insight into the reaction mechanism [1–3]. The activation and reaction volumes can be estimated from the dependences of the rate constant (k) or the equilibrium constant (K) of the reaction on external pressure (p) at constant temperature, using Eqs. (1) and (2):

$$(d\ln k/dp)_T = -1/RT(d\Delta G^{\neq}/dp)_T = -\Delta V^{\neq}/RT, \quad (1)$$

$$(d\ln K/dp)_T = -1/RT(d\Delta G/dp)_T = -\Delta V^0/RT. \quad (2)$$

It is well known that the activation and reaction volumes of ionic or highly polar reactions considerably vary with solvent polarity. Experimental evidence for the electrostriction of solvent molecules near ions is provided by decreased molar volumes of a series of salts, acids, and bases in solutions; moreover, as found in [4, 5] from solution density data, some salts have negative partial molar volumes. The termodynamic equations (1) and (2) are based on the assumption that at constant temperature the dependences of the free energies of activation and reaction at constant temperature on external pressure are determined by the contribution $p\Delta V$ at invariable effects on the free energies of other properties of the system. Increasing external pressure affects the density, viscosity, dielectric constant, and refractive index of a real liquid. Therefore, one should take into account that if the rate or equilibrium of a reaction are highly medium-dependent then the volume characteristics estimated by Eqs. (1) and (2) may not be very exact [6–9]. Thus, increasing pressure may accelerate reactions in low-viscosity media (Fig. 1, plot *1*) and decelerate the same reactions in more viscous media of the same polarity (Fig. 1, plot *4*). This fact can be explained by the imposition of diffusion control (Fig. 1, plot *2*) on the rates of such reactions in viscous media [8, 9].

A more complicated pattern is observed in ionic or highly polar processes. In terms of the transition state theory which includes a thermodynamic treatment of activation parameters, the rate constant of a reaction and its pressure dependence are determined by Eqs. (3) and (4) [10–12].

$$k = (RT/Nh)K^{\neq}(\gamma_A\gamma_B/\gamma^{\neq}), \quad (3)$$

$$(d\ln k/dp)_T = -\Delta V^{\neq}/RT + [d\ln(\gamma_A\gamma_B/\gamma^{\neq})/d_p]_T. \quad (4)$$

Here $K^{\neq}$ is the thermodynamic equilibrium constant between reagents A and B and transition state $X^{\neq}$ in infinitely dilute solution and γ_i are the activity coefficients of the corresponding states in the solution.

The activation volume ($\Delta V^{\neq}$) at usual pressure is equal to a difference in the partial molar volumes of the transition state and the reagents. This activation volume includes structural and solvation contributions, and it can experimentally be determined only from the pressure dependence of the free activation energy (Fig. 1, plot *1*). For ideal solutions at fixed temperatures, Eqs. (1) and (2) provide reliable volume characteristics. By contrast, for real solutions one should take account of the possible contribution in the pressure-induced free energy change of changes in activity coefficients [Eq. (4)]. The rates of nonpolar reactions are usually only slightly sensitive to properties of the medium (for instance, to ε), and, therefore, the second term in Eq. (4) is small. The equation for the electrostriction volume (ΔV_{el}) of a solvent with dielectric constant ε around charge q has been proposed in [13] [Eq. (5)]:

$$\Delta V_{\mathrm{el}} = (Nq^2/2b)[d(1/\varepsilon)/dp]_T. \tag{5}$$

The description of the free energy of charge transfer from vacuum to a surrounding continuum with dielectric constant ε has been theoretically substantiated in [14] [Eq. (6)]:

$$\Delta G_{\mathrm{el}} = -[Nq^2/2b][(\varepsilon - 1)/\varepsilon]. \tag{6}$$

Here b is the radius of the sphere encompassed by the surrounding continuum and N is the Avogadro number. From Eq. (6) it follows that the energy of electrostatic stabilization increases with increasing dielectric constant of the medium. At the same time, Eq. (5) expects increase in solvent electrostriction with decreasing dielectric constant. This is explained by the fact that $[d(1/\varepsilon)/dp]_T$ sharper decreases with pressure in media with lower dielectric constants. The transfer from the initial state to a polar transition state at atmospheric pressure already has an activation volume (Fig. 1, plot *1*), no matter whether ε changes with pressure or not. This activation volume can be determined by Eq. (1) on condition that solvent properties are unchanged $[(d\Delta G^{\neq}/dp)_{T,\varepsilon,\nu,\rho}]$ or estimated with small errors on condition that the process in hand is weakly sensitive to pressure-induced changes in the properties of the medium [6–9]. The effect of the medium on the rates of polar and ionic reactions is frequently described in terms of Eq. (7):

$$\Delta G^{\neq} = a + b(1/\varepsilon). \tag{7}$$

Here a and b are constants. Further decrease in the free activation energy of a polar reaction, produced by the pressure-induced increase in the dielectric constant of the medium (Fig. 1, plot *3*), gives rise to increased slope of the pressure dependence of the free energy of activation (Fig. 1, plot *5*) [7]. In other words, the activation volume of a polar reaction is only partly contributed by the pressure-induced change in the activation energy $(d\Delta G^{\neq}/dp)_T$. More illustrative examples of such superpositions of effects one can find by following changes in the free activation energy of fast reactions under pressure in high-viscosity media, where such changes are complicated by diffusion control [8, 9], or of changes in the measured free activation energy in reactions with strong intermolecular interactions between the reagents [15, 16], where reaction rate decreases with temperature, i.e. in such intricate processes in which the parameter studied changes sign. The fact that this problem in the determination of the volumes of polar and ionic reactions [Eqs. (1) and (2)] is not so obvious can be explained by that $(d\Delta G^{\neq}/dp)_T = c$, $[d(1/\varepsilon)/dp]_T$ from Eq. (7) change in the same direction as the partial molar volumes of ions in solutions of alkali metals salts or zwitter ions (for instance, amino acids) in a series of solvents with different dielectric constants [4, 5]. The change in the volume of the dissociation of a molecule into solvated ions in a series of solvents fairly correlates with the compressibility factors of the media [5], while the pressure-induced changes in the density of solvents determine changes in ε [17]. It should be noted the experimental forward and backward activation volumes of an equilibrium process with nonpolar initial and final states and a polar activated complex may be overestimated in absolute values, but their difference will be equal to the reaction volume determined independently from the partial molar volumes of the reagents and products at normal pressure.

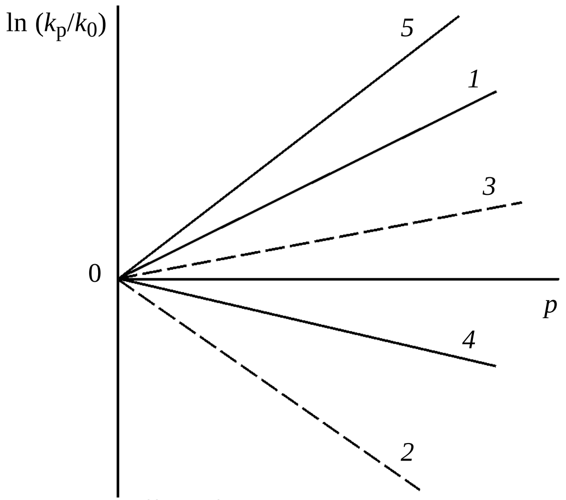


Fig. 1. (*1*) Effect of external pressure (p) on reaction rate [(ln(k_p/k_0)] at invariable solvent properties; (*2*) effect on reaction rate of pressure-induced change in solvent viscosity under diffusion control; (*3*) effect on reaction rate of pressure-induced change in solvent dielectric constant for polar reactions; and (*4*) and (*5*) total effects for polar reactions: $(\Delta V_1^{\neq} + \Delta V_2^{\neq}) = \Delta V_4^{\neq}$ and $(\Delta V_1^{\nu} + \Delta V_3^{\neq}) = \Delta V_5^{\neq}$.

Diels–Alder reactions are commonly weakly sensitive to solvent polarity and, consequently, to pressure-induced changes in ε. Recently we showed that the volumes of the nonpolar Diels– Alder reactions of

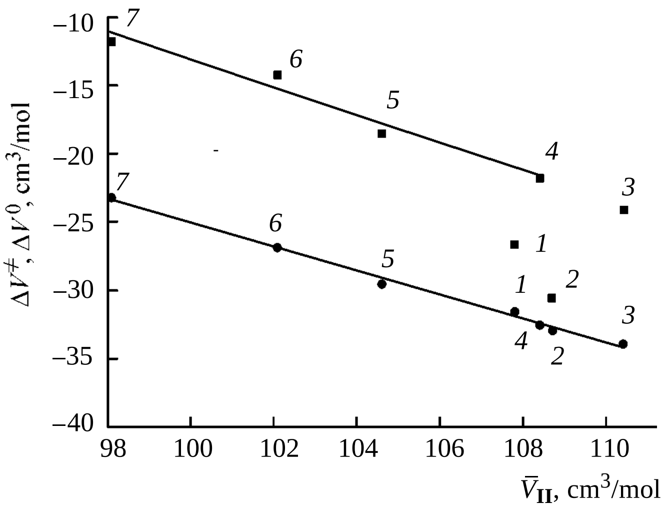


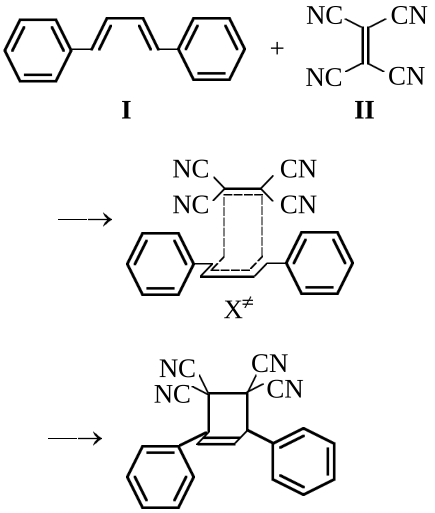
Fig. 2. (Circles) Activation volumes ($\Delta V^{\neq}$) of the Diels–Alder reaction of dienophile **II** with diene **I** and (squares; the ordinates of the points are shifted upward by 10 cm^3/mol) the reaction volumes (ΔV^0) of dienophile **II** with cyclopentadiene against the partial molar volumes of tetracyanoethylene ($\bar{V}_{II}$) in various solvents. The numbering of solvents is the same as in Table 2.

tetracyanoethylene with cyclopentadiene [18] and 9-chloroanthracene [19] are strongly affected by specific interactions of the reagents with solvents. Strong interactions of a π-donor solvent and the π-acceptor tetracyanoethylene (E_a 2.88 eV [20]) proportionally affect the solvation enthalpy and the partial molar volume of tetracyanoethylene [21]. Since the reaction adduct does not possess π-acceptor properties, then its solvation enthalpy and partial molar volume are already weakly dependent on π-donor properties of solvent, resulting in considerable changes in the reaction volume over a series of solvents. For the equilibrium reaction of tetracyanoethylene with 9-chloroanthracene in a series of solvents the reaction volumes were calculated from the pressure dependence of the equilibrium constant. The volumes of the nonequilibrium reaction of tetracyanoethylene with cyclopentadiene were determined directly from the difference in the partial molar volumes of the reagents and adduct. The sharp increase in the volume of the latter reaction in going from benzene (–32.0 cm^3/mol) to mesitylene (–21.8 cm^3/mol) is nicely consistent with the corresponding change in the partial molar volume of tetracyanoethylene (108.4 and 98.1 cm^3/mol in benzene and mesitylene, respectively) [21].

The changes in the enthalpies of solvation of the transition state of the Diels–Alder reaction with tetracyanoethylene, calculated from the Born cycle [22], showed that the enthalpy level of the activated compex in a series of π-donor solvents is almost invariable. For this reason, one can expect considerable changes in activation volumes for the reactions involving tetracyanoethylene over a series of solvents appreciably differing in π-donor properties. The effect of the medium on the activation and reaction volumes of Diels–Alder reactions has been studied in [23], but the reagents used (isoprene and maleic anhydride) are incapable of appreciable specific interactions with solvents. The Diels–Alder reactions of tetracyanoethylene with most dienes are very fast [24], which complicates kinetic studies at elevated pressures. We chose the reaction of *trans,trans*-1,4-diphenyl-1,3-budadiene (**I**) with tetracyanoethylene (**II**) (see the scheme below) because it gives a fairly stable adduct **III**, and the rate of this reaction is much reduced by the increased conjugation energy in the diene [24].

The resulting data are listed in Table 1.

Table 2 compares the solvent effects on the partial molar volume of tetracyanoethylene, on the activation volume of the reaction studied, and on the volume of the Diels–Alder reaction of tetracyanoethylene with cyclopentadiene.



As seen from the data in Table 2, the enthalpies of solution of tetracyanoethylene, its partial molar volumes, as well as the activation and reaction volumes in aromatic solvents vary in parallel. Correlating the volume characteristics (Fig. 2) leads to Eqs. (8) and (9):

$$\Delta V^{\neq} = (64\pm3) - (0.895\pm0.029)\bar{V}_{II};\ r\ 0.9974,\ n\ 7,\ s\ 0.3076, \quad (8)$$

$$\Delta V^{0} = (79\pm11) - (1.029\pm0.053)\bar{V}_{II};\ r\ 0.9846,\ n\ 4,\ s\ 0.7910. \quad (9)$$

Table 1. Effect of external pressure on the rate constant of the Diels–Alder reaction between diene **I** and dienophile **II** at 25°C[a]

p, kg/cm^2	$k_2\times 10^3$, l mol^{-1} s^{-1}	$-\ln k_2$	p, kg/cm^2	$k_2\times 10^3$, l mol^{-1} s^{-1}	$-\ln k_2$	p, kg/cm^2	$k_2\times 10^3$, l mol^{-1} s^{-1}	$-\ln k_2$	p, kg/cm^2	$k_2\times 10^3$, l mol^{-1} s^{-1}	$-\ln k_2$
1,2-Dichloroethane; $c_{\mathbf{I}}$ 3.01×10^{-4}, $c_{\mathbf{II}}$ 4.50×10^{-3} M, λ 27780 cm^{-1}						Benzene; $c_{\mathbf{I}}$ 2.51×10^{-2}, $c_{\mathbf{II}}$ 1.46×10^{-3} M, λ 22520 cm^{-1}					
0	95	2.35	620	209	1.56	0	6.97	4.97	390	11.7	4.45
160	111	2.20	705	232	1.46	0	7.27	4.92	460	13.4	4.31
230	132	2.25	770	260	1.35	220	9.88	4.62	550	14.7	4.22
330	147	1.92	805	268	1.32	330	11.0	4.51	620	15.7	4.15
445	176	1.74	975	319	1.14						
$\ln k_2 = (-2.344\pm 0.018) + (1.260\pm 0.011)\times 10^{-3}p$; r 0.9972, n 10, s 0.0303, $\Delta V^{\neq}$ -31.7 ± 0.3 cm^3/mol						$\ln k_2 = (-4.940\pm 0.015) + (1.298\pm 0.014)\times 10^{-3}p$; r 0.9970, n 8, s 0.0237; $\Delta V^{\neq}$ -32.7 ± 0.4 cm^3/mol					
Acetonitrile; $c_{\mathbf{I}}$ 4.70×10^{-4}, $c_{\mathbf{II}}$ 7.64×10^{-3} M, λ 27900 cm^{-1}						Toluene; $c_{\mathbf{I}}$ 7.41×10^{-2}, $c_{\mathbf{II}}$ 1.45×10^{-3} M, λ 23000 cm^{-1}					
0	79	2.54	510	165	1.80	0	2.56	5.97	630	5.01	5.30
210	102	2.28	605	176	1.74	0	2.61	5.95	770	6.34	5.06
310	124	2.09	755	212	1.55	300	3.54	5.64	980	8.34	4.79
410	141	1.96	905	259	1.35	500	4.71	5.36			
$\ln k_2$ $(-2.522\pm 0.020) + (1.312\pm 0.013)\times 10^{-3}p$; r 0.9971, n 8, s 0.0297; $\Delta V^{\neq}$ -33.1 ± 0.3 cm^3/mol						$\ln k_2 = (-5.972\pm 0.021) + (1.175\pm 0.014)\times 10^{-3}p$; r 0.9970, n 7, s 0.0345; $\Delta V^{\neq}$ $-29.6-0.4$ cm^3/mol					
Cyclohexanone; $c_{\mathbf{I}}$ 3.01×10^{-2}, $c_{\mathbf{II}}$ 2.60×10^{-3} M λ 25130 cm^{-1}						*o*-Xylene; $c_{\mathbf{I}}$ 1.72×10^{-2}, $c_{\mathbf{II}}$ 4.05×10^{-3} M, λ 18530 cm^{-1}					
0	14.2	4.25	415	27.4	3.60	0	1.08	6.83	580	2.09	6.17
0	14.1	4.26	625	32.5	3.43	150	1.24	6.69	700	2.38	6.04
150	16.5	4.11	750	36.3	3.32	175	1.31	6.64	825	2.71	5.91
175	17.2	4.06	950	51.7	2.96	270	1.53	6.48	825	2.55	5.97
310	22.2	3.81				495	1.82	6.31	985	3.03	5.80
$\ln k_2 = (-4.260\pm 0.026) + (1.346\pm 0.018)\times 10^{-3}p$; r 0.9938, n 9, s 0.0510; $\Delta V^{\neq}$ -34.1 ± 0.5 cm^3/mol						$\ln k_2 = (-6.818\pm 0.018) + (1.067\pm 0.010)\times 10^{-3}p$; r 0.9962, n 10, s 0.0314; $\Delta V^{\neq}$ -26.9 ± 0.3 cm^3/mol					
						Mesitylene; $c_{\mathbf{I}}$ 8.86×10^{-2}, $c_{\mathbf{II}}$ 1.80×10^{-3} M, λ 18150 cm^{-1}					
						0	0.217	8.44	705	0.395	7.84
						320	0.284	8.17	800	0.440	7.73
						500	0.356	7.94	970	0.485	7.63
						$\ln k_2 = (-8.476\pm 0.037) + (9.180\pm 0.235)\times 10^{-4}p$; r 0.9903, n 6, s 0.0453; $\Delta V^{\neq}$ -23.2 ± 0.6 cm^3/mol					

[a] $c_{\mathbf{I}}$ and $c_{\mathbf{II}}$ are the initial concentrations of the reagents and λ is the working wavelength.

The slope of Eq. (9) is equal to one, which corresponds to a complete loss of π-acceptor properties in the adduct. This conclusion is consistent with the data in [18], which point to a weak effect of aromatic solvents on the heats of solution and the partial molar volume of the adduct of the cyclopentadiene with tetracyanoethylene.

The slope of Eq. (8) suggests that only a small part (~0.1) of the π-acceptor capacity of tetracyanoethylene is preserved in the activated complex. As seen from Table 2, in nonaromatic solvents the reaction volume does not change proportionally with the partial molar volume of tetracyanoethylene. Since the partial molar volume of cyclopentadiene in all the solvents (Table 2) changes only slightly, the deviation observed for nonaromatic solvents (Fig. 2, plot *2*) should be related to some specific medium effects on the

Table 2. Medium effects on the enthalpies of solution of tetracyanoethylene ($\Delta H_{\mathbf{II},\mathrm{sol}}$), its partial molar volumes ($\bar{V}_{\mathrm{II}}$), the activation volume ($\Delta V^{\neq}$) of the Diels–Alder reaction between dienophile **II** and diene **I**, and the reaction volume of dienophile **II** with cyclopentadiene at 25°C

No.	Solvent	$\bar{V}_{\mathbf{II}}$[a], cm^3/mol	$-\Delta V^{\neq}$, cm^3/mol	$-\Delta V^{0\mathrm{a,b}}$, cm^3/mol	$\Delta H_{\mathbf{II},\mathrm{sol}}$[a], kJ/mol
1	1,2–Dichloroethane	107.7	31.7	36.8	21.3
2	Acetonitrile	108.7	33.1	40.7	15.2
3	Cyclohexanone	110.4	34.1	34.3	7.6
4	Benzene	108.4	32.7	32.0	14.9
5	Toluene	104.6	29.6	28.6	9.7
6	*o*-Xylene	102.1	26.9	24.3	1.4
7	Mesitylene	98.1	23.2	21.8	–2.7

[a] Data of [18]. [b] The reaction volume was not estimated from the difference in the molar volumes of adduct **III** and reagents **I** and **II** because of the poor solubility of adduct **III** in aromatic solvents.

partial molar volume of the adduct. According to [7, 18], accessibility for interaction with solvents of internal (two tertiary and two quaternary) carbon atoms in the branched adduct depends strongly on the volume and structure of the solvent, which determines the volume of cavities in the adduct, inaccessible for solvation. As a result, the partial molar volume of the adduct undergoes considerable changes even in media where no specific interactions are possible. On the other hand, a high correlation coefficient [Eq. (8)] is observed with all the solvents studied. Thus, the transition state has structure $X^{\neq}$, where approach of solvents is not yet hindered, but the ability of the tetracyanoethylene fragment to specific interactions with π-donor solvents is sharply weakened.

The resulting data are the first example of a considerable effect of the medium on the activation volume of a nonpolar reaction. These results allow us to expect appreciable medium effects on activation and reaction volumes for ionic, polar, low-polarity, and nonpolar reactions, where there is a strong interaction of the solvent with one of the two states of the reaction.

From the activation volumes of the reaction studied in aromatic solvents we cannot decide between two reaction pathways: involving free tetracyanoethylene molecules or involving the complex of tetracyanoethylene with the solvent. In the first case, increased pressure should raise the apparent rate constant to a lesser degree, because the fraction of free tetracyanoethylene molecules is descreased by increased equilibrium constant of the complex between tetracyanoethylene and the π-donor solvent. In this case, the apparent activation volume is equal to the difference in the activation volumes of the reagents in an inert medium and the formation volume of tetracyanoethylene with the aromatic solvent. In the second case, the apparent activation volume corresponds to transition from complexed tetracyanoethylene whose fraction is 0.97. Quantitative relationships for the two pathways have one and the same starting point and, therefore, are identical to each other. This conclusion remains valid for the reaction performed under pressure in a mixture of an inert and a π-donor solvent.

EXPERIMENTAL

trans,trans-1,4-Diphenyl-1,3-butadiene (**I**) was purified by recrystallization from ethanol, mp 150–151°C (149–150°C [25]). Tetracyanoethylene (**II**) (Merck) was sublimed in a vacuum (~50 Pa) at 110°C, mp 200–201°C (201–202°C [26]. All solvents were purified by known procedures [27]. Adduct **III** was obtained from equimolar solutions of reagents **I** and **II** in 1,2-dichloroethane, followed by recrystallization from benzene, mp 211–212°C (211–212°C [28]).

Before kinetic measurements we chose an optimal working spectral range, where one of the reagents absorbs rather strongly and the second reagent and the adduct absorb weakly (Table 1). The reaction progress in nonaromatic solvents was followed by the absorbance of diene **I**, using a large excess of dienophile **II**, while in aromatic solvents, by the absorbance of the complex of dienophile **II** with the solvent, using a large excess of diene **I**. It was found that the pressure range studied the reagent absorbances fit the Beer law. The concentration of a compound taken in excess was always 10 times higher that the concentration of a compound whose absorbance was used for rate measurements. The second-order rate constants (k_2) were calculated by Eq. (10):

$$k_2\tau = 1/c_i \ln (D_0/D_\tau). \qquad (10)$$

Here τ is time, c_i is the concentration of a reagent taken in excess, and D_0 and D_τ are the initial and current absorbances. The reaction completeness was 40–80%. The correlation coefficients for all the rate constants were higher than 0.999.

The design and operation of the barostat and the high-pressure unit with a variable-volume quartz cell (Specord UV-Vis spectrophotometer) have been described in [7, 29]. The new design of the cylinder, which allows complete isolation of the oil fed under pressure from a transparent liquid (octane) transferring pressure to the instrument cell, makes possible spectral measurements in the UV range without contamination of the octane even at multiple measurements. The necessity in choosing conditions providing pseudo-first-order reaction conditions stems from the fact that at concentrations ensuring optimal reagent absorbances the reaction half-time was 0.5 to 4 h. The initial reaction period (5–7 min) after raising the pressure is required for relaxation of the temperature jump produced by solution compression, and, therefore, this period should not be taken into account in calculating rate constants. The reaction was performed in a quartz cell (l 1 cm), whose neck was thoroughly ground in the base of a cylindrical glass tube. The base of this tube had a thin capillary for communicating the cell with the upper cylinder. The cell was charged with a reaction mixture and tightly stopped with the cylindrical tube which then filled with mercury for equalizing the pressure in the operation mode. All solvents were checked for constant absorbances of the components in the presence and in the absence of mercury. The initial transmittance of the temperature-controlled (25 ± 0.1°C) high-pressure unit with a solvent-filled cell (T 100%) was set by smoothly aligning the diaphragm fixed in the cell compartment on the path of the reference beam. After that the high-pressure unit was taken out from the cell compartment, and one more diaphragm was placed on the path of the working beam, aligned to the initial transmittance (T 100%), and taken away, after fixing its orifice diameter, from the special holder. At prolonged measurements (more than 1–2 h) the high-pressure unit was temporarily taken out of the cell compartment, the latter diaphragm was placed on the path of the working beam, and testing for possible variations in the dark current was performed. In most experiments no corrections were required in optical density calculations.

In all the calculations the concentrations of the compounds were assumed pressure-independent.

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