Diffusion control of the Diels—Alder reaction rate at elevated pressures

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The influence of the temperature and external pressure on the rate of the Diels—Alder reaction between 9,10-dimethylanthracene and maleic anhydride was studied in the series of solvents with wide intervals of viscosity (0.3—43.2 mPa s), dielectric constant (2—38), and internal pressure (3—8.8 kbar). At a standard pressure these properties of the solvent exert a weak and irregular effect on the reaction rate constant and activation enthalpy and entropy. The effect of the external pressure on the rate constant was studied in a high-pressure (up to 1 kbar) optical cell in acetonitrile and silicon oil and in a barostat cell (up to 6 kbar, toluene, silicon oil). Close values of the activation volume were obtained in all solvents. In toluene the reaction rate increases smoothly in the whole pressure interval. In more viscous silicon oil a similar dependence is observed up to 3 kbar, and the reaction rate decreases sharply with the further increase in the pressure and viscosity because of the diffusion control of the process.

Key words: Diels—Alder reaction, kinetics, external pressure, activation volume, viscosity effect, diffusion control.

Elevated pressures found wide use in organic synthesis.[1] For processes accompanied by a decrease in the volume on going from the reactants to the activated complex ($\Delta V^{\neq}$) and then to the products (ΔV_0), an elevated external pressure (p) results in an increase in the rate (k) and equilibrium (K) constants according to the following correlations[1—4]:

$$(\partial \ln k/\partial p)_T = -1/RT(\partial G^{\neq}/\partial p)_T = -\Delta V^{\neq}/RT, \qquad (1)$$

$$(\partial \ln K/\partial p)_T = -1/RT(\partial G_0/\partial p)_T = -\Delta V_0/RT, \qquad (2)$$

where $G^{\neq}$ and G_0 are the free energies of the activation and reaction, respectively.

Reliability of correlations (1) and (2) has recently been confirmed for the equilibrium Diels—Alder reaction between 9-chloroanthracene and tetracyanoethylene: the close values of the reaction volumes were obtained from the dependence of the equilibrium constant on the external pressure (Eq. (2)), difference in the activation volumes of the direct and reverse processes (Eq. (1)), and difference in the partial molar volumes of the products and reactants.[5] An additional information on the activation volumes makes it possible to arrive at a more substantiated concept of the reaction mechanism.[2—7] It should be noted that an increase in the temperature and pressure always results in the opposite change in such properties of the medium as the density, dielectric constant, and viscosity. In polar and ionic processes with a high sensitivity of the rate to a change in the dielectric

constant, an elevated pressure can affect the rate due to both the mechanical work ($p \cdot \Delta V^{\neq}$) and a change in the solvent polarity under the pressure.[6,7]

A slight increase in the Diels—Alder reaction rate constant has recently[8,9] been observed for the dimerization of 1,3-cyclopentadiene under standard pressure in the series of *n*-alkanes. A possible increase in the rate of this reaction in a more viscous medium was explained in the framework of the positive cage effect of the solvent for the activation process with a negative entropy. Since the viscosity of organic solvents increases with the pressure increase, it is assumed[9] that the experimental dependence of the Diels—Alder reaction rate on the external pressure (Eq. (1)) also includes an additional ("phantom") contribution, which is not related to the activation volume $\Delta V^{\neq}$. This rationale[9] was criticized.[10] The rate of cyclopentadiene dimerization in a series of *n*-alkanes has recently[11] been measured repeatedly to show that the reaction rate changes insignificantly and irregularly with the viscosity increase.

However, the increase in the solvent viscosity induced by the external pressure can achieve a diffusion control level. Under standard conditions (25 °C, 1 bar), the viscosity of organic solvents is sufficiently low being only $(3—30) \cdot 10^{-4}$ Pa s. The diffusion rate in standard media can exert a noticeable effect only on fast processes[12,13] with the relaxation time of an order of 10^{-8}—10^{-10} s. Many facts are known when the observed rates of ionic reactions and photoinduced fast monomolecular

cis—trans-isomerization processes decrease with an increase in the viscosity in the solvent series or under high pressures.[12−15] For the consecutive bimolecular process

$$A\|B \xrightarrow{k_D} A + B \xrightarrow{k_{TST}} A—B, \qquad (3)$$
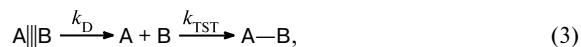
in which the first step reflects the rate of approaching solvent-separated reactants (k_D) and the second step corresponds to the structural rearrangement of bonds in the framework of the classical transition state theory (k_{TST}), the observed rate constant (k_{obs}) is described[12,14] by correlation (4)

$$1/k_{obs} = 1/k_D + 1/k_{TST}. \qquad (4)$$

In standard solvents k_D is high (10^8—10^{10} L mol^{-1} s^{-1}) and considerably exceeds the k_{TST} value, which almost corresponds for this reason to the experimentally observed k_{obs} value.

The purpose of this work is to reveal conditions of the Diels—Alder reactions in solutions under elevated pressures at which the solvent viscosity can affect the moderate rate of the process. The reaction of 9,10-dimethylanthracene (**1**) with maleic anhydride (**2**) (Scheme 1), being convenient for spectrophotometric monitoring of the rate, was studied in solvents, whose viscosity differed more than 100-fold under standard conditions.

Since an elevated pressure induces the dielectric constant (ε) growth, it was necessary to elucidate the influence of this characteristic of the solvent on the reaction rate. As can be seen from the data in Table 1, no correlation is observed between the changes in the reaction rate, enthalpy ($\Delta H^{\neq}$), and entropy ($\Delta S^{\neq}$) and changes in the dielectric constant and viscosity (η) of the solvent. The influence of the internal pressure of solvents (p_{int}), which

Scheme 1
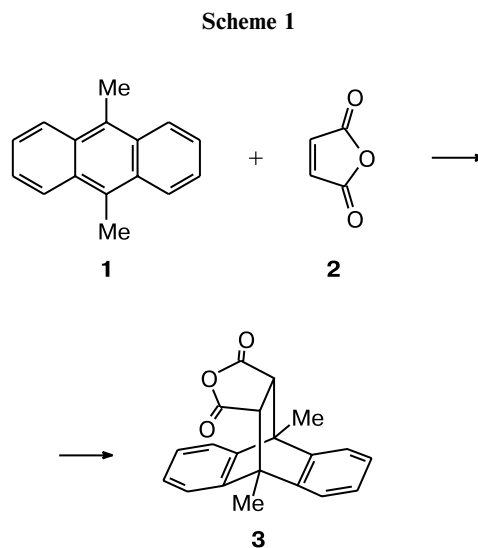
is equal to $\Delta H_{vap}/V$ (ΔH_{vap} is the evaporation enthalpy, and V is the molar volume of the liquid) on the kinetic parameters of the reaction is not observed either.

The data on the heats of solution (ΔH_{sol}) of reactants **1** and **2** and activation enthalpies (Table 2) make it possible to calculate the changes in the enthalpy of solvation of the reactants ($\delta H_{solv}^{reac}(S/S_0)$) and transition state ($\delta H_{solv}^{TS}(S/S_0)$) relatively to the reference solvent (S_0)

$$\delta H_{solv}^{TS}(S/S_0) = \delta H^{\neq}(S/S_0) + \delta H_{solv}^{reac}(S/S_0). \qquad (5)$$

Therefore (see Table 2), the differences in the activation enthalpy of the reaction in the media studied are caused by the changes in the enthalpies of solvation of both reactants and transition state.

Since the partial molar volumes of 9,10-dimethylanthracene (187 ± 1 cm^3 mol^{-1}) and maleic anhydride

Table 1. Rate constants (k_2), activation enthalpies ($\Delta H^{\neq}$), and activation entropies ($\Delta S^{\neq}$) of the Diels—Alder reaction between 9,10-dimethylanthracene and maleic anhydride in solvents with different viscosities (η), dielectric constants (ε_{20}), and internal pressures (p_{int}) at 25 °C

Solvent	$k_2 \cdot 10^3$ /L mol^{-1} s^{-1}	$\Delta H^{\neq}$ /kJ mol^{-1}	$-\Delta S^{\neq}$ /J mol^{-1} K^{-1}	η /mPa s	ε_{20}	p_{int} /kbar
Cyclohexane	63.6	30.1	167	0.894	2.02	2.98
1,4-Dioxane	12.0	41.0	144	1.117	2.22	4.28
CCl$_4$	46.7	32.6	161	0.908	2.24	3.27
CHCl$_3$	70.0	31.8	160	0.537	4.81	3.71
Benzene	21.6	37.7	150	0.604	2.28	3.71
Toluene	15.0	37.7	151	0.560	2.38	3.48
Chlorobenzene	45.2	32.6	161	0.753	5.69	3.86
Nitrobenzene	25.0	36.8	152	1.863	35.6	4.80
Nitromethane	30.2	33.5	161	0.630	37.27	6.96
MeCN	25.8	36.0	155	0.369	36.64	6.21
DMF	11.1	42.3	140	0.794	38.25	6.02
AcOH	28.5	41.4	135	1.056	6.20	8.87
Acetone	9.2	44.8	133	0.306	21.01	4.08
Silicon oil	41.0	43.3	127	43.2	—	—

Table 2. Enthalpies of solution (ΔH_{sol}) of 9,10-dimethyl-anthracene (**1**) and maleic anhydride (**2**) and changes in the enthalpies of solvation of the reactants (δH_{solv}^{reac}) and transition state (δH_{solv}^{TS}) relatively to acetone at 25 °C

Solvent	ΔH_{sol}/kJ mol^{-1}		δH_{solv}^{reac}	δH_{solv}^{TS}
	1	**2**		
Cyclohexane	29.8	36.4	29.7	15.0
1,4-Dioxane	23.1	10.4	−3.0	−6.7
CCl$_4$	23.6	24.9	12.0	−0.1
CHCl$_3$	20.0	16.1	−0.4	−13.3
Benzene	23.4	16.9	3.8	−3.3
Toluene	21.8	16.4	1.7	−5.6
Chlorobenzene	21.4	18.3	3.2	−9.0
Nitrobenzene	21.3	14.2	−1.0	−8.9
Nitromethane	30.4	12.6	6.5	−4.8
MeCN	28.9	13.1	5.5	−3.3
DMF	21.4	8.1	−7.0	−9.5
AcOH	23.7	15.0	2.2	−1.2
Acetone	25.2	11.3	0	0

(70.0±0.2 cm^3 mol^{-1} in MeCN) planar molecules are different, a much higher degree of desolvation at the achievement of the transition state can be expected for dienophile **2** than for diene **1**. For these reactants, the changes in the enthalpy of solvation in the studied series of solvents are not proportional, and for maleic anhydride they are much higher (28.3 kJ mol^{-1}) than those for diene (10.4 kJ mol^{-1}). As a result, the complete absence of a correlation between the activation enthalpy, entropy, and free energy of the reaction and the enthalpy of solvation of diene is observed in the series of solvents (correlation coefficient $r \leq 0.11$), whereas for dienophile this dependence is more pronounced ($r \geq 0.72$). The correlation of the activation enthalpy and free activation energy in these media ($r = 0.91$) excludes CHCl$_3$ and AcOH capable of forming hydrogen bonds. When they are ignored, the compensation effect is manifested very distinctly ($r = 0.985$). The absence of the influence of the dielectric constant of the medium on the reaction rate makes it possible to rule out a possibility of changing the rate because of an increase in ϵ at an elevated pressure.

Despite more than a 100-fold increase in the viscosity for silicon oil, the rate constants and activation parameters in this medium differ weakly from the data in other solvents (see Table 1). However, differences in the solvation enthalpy in the series of solvents can overlap the influence of the medium viscosity on the reaction rate. A more reliable conclusion about the viscosity effect can be obtained from comparison of the effect of the elevated pressure on the rate of the process in solvents with strongly different viscosities. The method for studying reaction rates at an elevated pressure has a unique possibility to change the viscosity of the same solvent in a wide interval at a constant temperature. The degree of changing of

many properties of solvents (density, compressibility, refraction index, dielectric constant) decreases with the pressure increase. The only exception is viscosity. It is known[16—18] that this parameter increases according to an exponential law with the pressure increase

$$\eta_p = \eta_{p=1} \cdot e^{\alpha p}, \qquad (6)$$

where η_p and $\eta_{p=1}$ are the viscosities at an elevated and standard (atmospheric) pressure, respectively.

In the high-pressure interval, the baric viscosity coefficient (α) does not decrease but increases. This tendency is especially pronounced for large molecules with a high viscosity under standard conditions.[14,16,17]

For the majority of organic solvents, at 25 °C the baric viscosity coefficient (α) ranges within $(3—6) \cdot 10^{-4}$ bar^{-1}, whereas for more viscous liquids the α coefficient is much higher[14,17] and can exceed $4 \cdot 10^{-3}$ bar^{-1}. Comparison of the α and η values for the series of viscous liquids[14,16,17] at 25 °C makes it possible to estimate the α value for silicon oil $((3±0.5) \cdot 10^{-3}$ bar$^{-1})$. When the pressure increases to 1 kbar, the viscosities of MeCN, toluene, and silicon oil increase by 1.4, 1.6, and 20 times, respectively. If the assumption[9] on the acceleration of the Diels—Adler reaction with the viscosity increase (cage effect) is valid, the effective activation volume should be more negative in more viscous silicon oil.

For studies of the pressure influence of the reaction rate at 25 °C, MeCN ($\epsilon_{20} = 36.5$, $\eta_{25} = 3.7 \cdot 10^{-4}$ Pa s),[19] toluene ($\epsilon_{20} = 2.38$, $\eta_{25} = 5.5 \cdot 10^{-4}$ Pa s),[19] and silicon oil ($\eta_{25} = 4.32 \cdot 10^{-2}$ Pa s) were chosen as solvents. The data for the reactions in MeCN and silicon oil obtained using a UV unit at pressures below 1 kbar are presented in Table 3. For the reactions in MeCN and silicon oil, the experimental plots of the rate *vs.* pressure are described by Eqs. (7) and (8), respectively

$$\ln(k_p/k_{p=1}) = (-9.6\pm15.8) \cdot 10^{-3} + (8.79\pm0.08) \cdot 10^{-4} \cdot p, \quad (7)$$

$r = 0.996$, $n = 10$;

$$\ln(k_p/k_{p=1}) = (5.0\pm10.8) \cdot 10^{-3} + (8.29\pm0.08) \cdot 10^{-4} \cdot p, \quad (8)$$

$r = 0.998$, $n = 10$.

The activation volumes in MeCN ($\Delta V^{\neq} = -22.5\pm1.5$ cm^3 mol^{-1}) and silicon oil ($\Delta V^{\neq} = -20.9\pm1.5$ cm^3 mol^{-1}) were calculated by Eqs. (7) and (8). The close values obtained for the activation volumes in silicon oil ($\eta_{p=1} = 43.2$ mPa s, $\eta_{p=1000} = 880$ mPa s) and MeCN ($\eta_{p=1} = 0.37$ mPa s, $\eta_{p=1000} = 0.54$ mPa s), whose viscosities differ by more than two and three orders at pressures of 1 bar and 1 kbar, respectively, do not agree with the assumption[9] on the possible additional acceleration of the Diels—Alder reaction (due to the enhancement of the cage effect of the solvent) with an increase in the viscosity of the medium.

Table 3. Influence of the pressure (p) on the rate constant (k_2) of the Diels—Alder reaction between 9,10-dimethylanthracene and maleic anhydride in MeCN and silicon oil at 25 °C

p/kg cm^{-2}	$k_2 \cdot 10^2$/L mol^{-1} s^{-1}	$\ln k_p/k_{p=1}$
	MeCN	
1	2.58	0
300	3.32	0.252
400	3.54	0.316
495	4.09	0.461
525	3.96	0.428
650	4.41	0.536
700	4.87	0.635
730	4.89	0.639
885	5.60	0.775
980	6.00	0.844
	Silicon oil	
1	4.10	0
270	5.22	0.241
300	5.21	0.240
330	5.47	0.288
525	6.43	0.450
595	6.92	0.523
625	6.95	0.528
695	7.39	0.589
790	7.96	0.663
930	8.78	0.762

In addition, if the diffusion rate in silicon oil is insufficient to maintain conditions provided by the transition state theory, the effective activation volume in this oil would be less negative. The data obtained assert that the diffusion rate (k_D) in silicon oil exceeds substantially the rate of bond rearrangement (k_{TST}) even at a pressure of 1 kbar.

The next cycle of measurements of the reaction rates was carried out at 25 °C and pressures below 6 kbar. The baric viscosity coefficient of silicon oil (($3\pm0.5)\cdot10^{-3}$ bar^{-1}) corresponds to an increase in the medium viscosity by 6—9 orders of magnitude at a pressure of 5—6 kbar. It has been established that silicon oil has a rather low vitrification temperature (-80—-90 °C). The results of micrometric measurements of its compressibility at 25 °C correspond to the liquid phase at a pressure of at least 7 kbar. Since MeCN is solidified under these conditions,[16] toluene ($\eta_{p=1} = 0.56$ mPa s, $\alpha = 5\cdot10^{-4}$ bar^{-1}), which is not solidified at 25 °C and the pressure below 9 kbar,[16] was chosen as a reference solvent. The smooth ($r = 0.998$) increase in the rate constants in toluene is observed in the whole studied interval of pressures (Table 4, Fig. 1)

$$\ln(k_p/k_{p=1}) = (-0.02\pm0.07) + (7.83\pm0.08)\cdot10^{-4}\cdot p -$$
$$- (3.12\pm0.58)\cdot10^{-8}\cdot p^2. \quad (9)$$

Table 4. Experimental (k_{obs}), classical (k_{TST}), and diffusional (k_D) rate constants of the Diels—Alder reaction between 9,10-dimethylanthracene and maleic anhydride at an elevated pressure (p) in silicon oil (SO) and toluene (Tol) at 25 °C

p /kg cm^{-2}	k_{obs}^{Tol}	k_{obs}^{SO}	k_{TST}^{SO}	k_D^{SO}	η_p^{SO} /Pa s
		L mol^{-1} s^{-1}			
1	0.015	0.041	0.041	—	0.043
500	0.022	0.054	0.056	—	0.19
1000	0.031	0.088	0.084	—	0.88
1500	0.044	0.12	0.12	—	4.0
2000	0.062	0.19	0.18	—	18
2500	0.086	0.27	0.24	—	80
3000	0.116	0.33	0.32	—	360
3500	0.156	0.34	0.40	2.3	1600
4000	0.205	0.26	0.54	0.50	$7.2\cdot10^3$
4500	0.266	0.15	0.71	0.19	$3.2\cdot10^4$
5000	0.340	0.062	0.91	0.066	$1.4\cdot10^5$
5500	0.427	0.015	1.14	0.015	$6.4\cdot10^5$
6000	0.529	0.0025	1.41	0.0025	$2.9\cdot10^6$

Note. η_p^{SO} is the viscosity of silicon oil at the indicated pressure.

The deviation from linearity (Eq. (1)) observed for the dependence described by Eq. (9) is caused by the difference in compressibilities of the partial molar volumes of the reactants and transition state.[20] The activation volume in toluene (-20 ± 2 cm^3 mol^{-1}) is close to the values obtained in MeCN and silicon oil.

The plots of the reaction rate *vs.* external pressure in silicon oil and toluene almost coincide in the interval from 0 to 3 kbar (see Table 4, Fig. 1). However, in the 3.5—6 kbar region, the observed rate constant in silicon oil (k_{obs}^{SO}) decreases sharply. Based on the experimental k_{obs}^{SO} values from correlation (4), we calculated the diffusion rate constants in silicon oil (k_D^{SO}). The data on the reaction rate constant at an elevated pressure in silicon
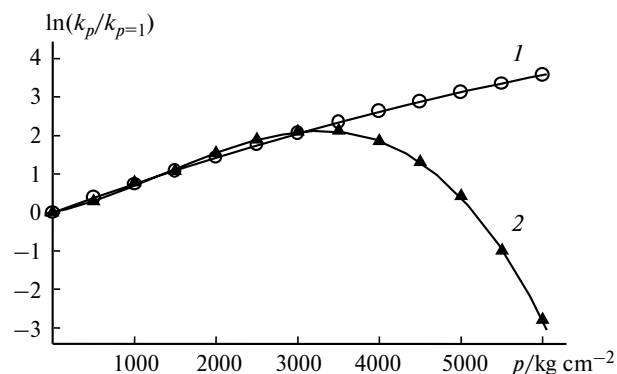
Fig. 1. Influence of the external pressure (p) on the rate constants (k/L mol^{-1} s^{-1}) of the Diels—Alder reaction of 9,10-dimethylanthracene with maleic anhydride in toluene (*1*) and silicon oil (*2*) at 25 °C.

oil, which are necessary for calculation and are expected in the framework of the transition state theory (k_{TST}^{SO}), were determined from the experimental dependence of the reaction rate on the pressure in toluene (Eq. (9)) using the $k_{p=1}$ value in silicon oil (0.041 L mol^{-1} s^{-1}). Since the experimental (k_{obs}^{SO}) and calculated (k_{TST}^{SO}) values almost coincide in the pressure interval below 3 kbar, the k_D^{SO} values were calculated for the pressure interval from 3.5 to 6 kbar (see Table 4).

The viscosity of silicon oil at an elevated pressure was calculated from Eq. (6) with the α coefficient equal to $3 \cdot 10^{-3}$ bar^{-1}. The calculation of the absolute values of the diffusion rate constants by the Smoluchowski equation[12] is not reliable, because the structure of the reactants are far from ball-like. The relative changes in the diffusion rate constants are determined by the ratio of the viscosity values

$$(k_D^{calc})_p/(k_D^{calc})_{p=1} =$$

$$= (\text{const} \cdot RT/\eta_p)/(\text{const} \cdot RT/\eta_{p=1}) = \eta_{p=1}/\eta_p. \quad (10)$$

Comparison of the values calculated from Eqs. (4) and (10) gives a linear dependence with the angular coefficient 1.13 ($r = 0.995$, $n = 6$) close to unity, which agrees with the diffusion control of the reaction under study in silicon oil at pressures of 3.5—6 kbar.

Changes in the reaction rate and solvent viscosity induced by an elevated pressure provide a very convenient method for checking conditions under which the kinetic transition state theory is fulfilled or violated. The results obtained indicate that for the moderate bimolecular Diels—Alder reaction in a medium with the viscosity below 500—1000 Pa s the number of active collisions is rather great and proportional to their concentration and, hence, the rate of the process is described in the framework of the transition state theory. With the further increase in viscosity, the number of collisions decreases so that the classical description of the process rate is inappropriate because of diffusion control. A similar viscosity level for standard organic solvents at 25 °C can be created by an external pressure of approximately 20—30 kbar. It is clear that for faster processes the viscosity and pressure threshold for diffusion control can be achieved at lower values. Similar observations are described for several solvolysis reactions.[21]

Virtually the same activation volume of the reaction studied in media with strongly different viscosities and baric coefficients excludes the positive (cage effect of the solvent) and negative (diffusion control) effects of the viscosity of the chosen solvents on the rate of the process (at least at a pressure below 3 kbar). Note that the absence of the positive cage effect rules out the bipolar and biradical mechanisms in the limiting step of this reaction.

Experimental

Reactants. After distillation, maleic anhydride (**2**) was sublimed *in vacuo*. The presence of even trace concentrations of maleic acid, which are poorly soluble in benzene, can easily be detected by the presence of a suspension. 9,10-Dimethyl-anthracene (**1**) (Aldrich) was purified by chromatography on a column (Al$_2$O$_3$, benzene—hexane (1 : 3) as eluent). The spectral purity of diene **1** and completeness of the reaction with a minor excess of dienophile **2** were checked by the absence of its absorption band in the region of $\lambda = 380—420$ nm for a period $\geq 7 \cdot \tau_{0.5}$ ($\tau_{0.5}$ is the half-period of the reaction). Solvents were purified by known methods.[22] The values of viscosity, dielectric constant, and internal pressure of solvents were taken from published data.[19] Silicon oil (DC-704 for diffusion pumps, b.p. 215 °C (50 Pa)), which is transparent in the region above 350 nm, was used without additional purification. The viscosity of silicon oil at 25 °C and an atmospheric pressure (43.2 mPa s) was determined by the dropping ball method using a Hoeppler viscometer, and its density (1.0643 g cm^{-3}) was determined on a DMA-602 precision densimeter. The smooth decrease in the volume of silicon oil was detected by the micrometric method with the pressure increase to 7 kbar at 25 °C in a barostat with a multiplier.

Kinetic measurements at a standard pressure were carried out at 25, 35, and 45 °C in a thermal unit placed in a cell compartment of the spectrophotometer. A high-pressure optical unit[5,7] was used for measurements at pressures below 1 kbar. The reaction rate in a cell with a variable volume placed in the high-pressure optical unit was monitored by a change in the absorption of diene **1** ($\lambda = 400—420$ nm), whose initial concentration was 20-fold lower than that of dienophile **2**. The reactions in toluene and silicon oil under pressures below 6 kbar were carried out in a Teflon cylinder in a barostat with pressure multiplication (25 : 1).[23] The temperature of the high-pressure cells (25±0.1 °C) was maintained using an external coil pipe attached to a thermostat. The concentrations of dienophile **2** (($1—3$) $\cdot 10^{-3}$ mol L^{-1}) exceeded the concentrations of diene **1** 15—20 times. The rate constants were calculated from the data on a change in the absorption of diene **1** in a solution under pressure. The degree of completion of the reaction was 50—70% for a period of 2—6 h. Solvents were not frozen and/or precipitates were not formed in the whole pressure interval.

The heat of solution of reactants was determined at 25 °C on a differential calorimeter by a previously described procedure.[24] The concentration of dissolved reactants did not exceed $3 \cdot 10^{-3}$ mol L^{-1}. At least three successive measurements of thermal effects of solution were carried out in all solvents except cyclohexane. The mean deviation did not exceed ±0.5 kJ mol^{-1}. Since the solubility of reactants **1** and **2** in cyclohexane are low, their enthalpies of solution were calculated by the assignment of the observed thermal effects to concentrations determined by titration.

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