Reactivity of 4-Phenyl-1,2,4-triazoline-3,5-dione and Diethylazocarboxylate in [4+2]-Cycloaddition and Ene Reactions: Solvent, Temperature, and High-Pressure Influence on the Reaction Rate

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ABSTRACT: We have studied the solvent, temperature, and pressure influences on the reaction rates of cyclic and acyclic N=N bonds in the Diels–Alder and ene reactions. The transfer from N-phenylmaleimide (**9**) to a structural analogue, 4-phenyl-1,2,4-triazoline-3,5-dione (**2**), is accompanied by the rate increase in five to six orders of magnitude in the Diels–Alder reactions with cyclopentadiene (**4**) and 9,10-dimethylanthracene (**5**), whereas the transfer from dimethyl fumarate (**10**) to diethyl azodicarboxylate (**1**) increases only in one to two orders of magnitude. The ratio of the reaction rate constants (**2** + **4**)/(**1** + **4**) is very large (5.2×10^7) and almost the same (5.3×10^7) as in the ene reactions with tetramethylethylene (**7**),

($\mathbf{2}$ + $\mathbf{7}$)/($\mathbf{1}$ + $\mathbf{7}$). It has been observed that the N=N bond in reagent $\mathbf{2}$ has strong electrophilic, and its N–N moiety in the transition state has nucleophilic properties, which results from the analysis of the solvation enthalpy transfer of reagents, activated complex, and adduct in the Diels–Alder reaction of $\mathbf{2}$ with anthracene $\mathbf{22}$. © 2015 Wiley Periodicals, Inc. Int J Chem Kinet 47: 289–301, 2015

INTRODUCTION

It is widely accepted that the Diels–Alder reactions (DAR) have commonly concerted, "aromatic" transition state with synchronous formation of both new C–C bonds. However, at the present time the possibility of implementing of all options of the DAR mechanism has been considered. The one-step one-stage synchronous mechanism of the bonds formation has been proven for the nonpolar DAR of symmetrical reagents as cyclopentadiene and ethylene with formation and decay of norbornene [1–4], as well as polar DAR with the large charge separation, such as a reaction of tetracyanoethylene with cyclopentadiene [4] and with 9,10-dimethylanthracene [5]. For the latter reaction between very strong π-donor diene and the strongest π-acceptor dienophile, the intermolecular interaction energy in a molecular complex between reagents is more than the subsequent activation energy for this reaction. Therefore, the observed activation energy is negative. This corresponds to the fact that the geometry of the molecular complex is similar to the geometry of the transition state of this reaction [5]. Note that the solvent effect on the rate of this polar reaction is determined by the hard deactivation of tetracyanoethylene in π-donor solvents. The rate constants (25°C) and dissolution enthalpies of solid tetracyanoethylene in trichloromethane, acetonitrile, benzene, toluene, o-xylene, and mesitylene are 260×10^3, 43.5×10^3, 8.5×10^3, 2.8×10^3, 0.82×10^3, 0.30×10^3 L mol^{-1} s^{-1} and 24.5, 15.2, 14.9, 9.7, 1.4, and -2.7 kJ mol^{-1}, respectively [5,6]. Overall, for all DAR involving asymmetric dienes and dienophiles should be expected for the asynchronous types of the bond formations via one-step two-stage biradical or bipolar transition states [3,7–10], and two-stage zwitterionic intermediate, when asymmetry of reagents is very large [4,10–12], and even via the ionic mechanism, as in the DAR of cyclopentadiene with the iminium cation [4]. The basis for the selection of the DAR mechanism is ab initio calculations, substituent effects on the rate, kinetic isotope effects, conservation/violation of stereospecificity, solvent effect on the rate, the values of entropy and volume of activation [3,4,9,10,12,13]. Most calculations have shown that the synchronous formation of new bonds is eas-

ily violated for asymmetric reagents, but the difference in the energy of the synchronous and asynchronous states can be small [1–4,7–10]. A calculated one-step two-stage mechanism has been proposed for the ene reactions [14]. The conservation of stereospecificity and the lack of the rate acceleration of two stage reactions in polar solvents can be explained by the shorter time between the formation of the first and second bond in the transition state, than the time required for the rotation around the C–C bond with violation of stereospecificity and for the solvent reorganization [3,4]. Only in few cases, the lifetime of an intermediate is sufficient to capture, for example, methanol molecules from the solution in the DAR [15], in violation of stereospecificity [11,16,17] and in the ene reactions with 4-substituted-1,2,4-triazoline-3,5-diones [18–20]. Data on the lifetime of bipolar intermediates can be expected from the femtosecond time-resolved investigations [1,2].

The DAR of azodicarboxylates with conjugated dienes [21–23] and ene reactions with olefins [24,25] as well as both types of these reactions [23,26] has been thoroughly studied. As it was established, the ene reactions can be considered as additive substitution with allylic hydrogen addition to the nitrogen atom accompanied by the obligated shift of the C=C double bond in olefins [25–30]. Numerous reactions were carried out in the mild conditions with the very active N=N bond of 4-substituted-1,2,4-triazoline-3,5-diones. The large kinetic isotope effect was observed in the ene reactions with cis-2-CH$_3$,3-CD$_3$-butene-2 [30], and the subsequent studies [15,18,31–35] confirmed the formation of aziridinium imide during the first reaction step. The conservation and violation of the reaction stereospecificity of E,E-, E,Z-, and Z,Z-hexa-2,4-dienes with 4-phenyl-1,2,4-triazoline-3,5-dione were discussed in detail in several papers [18,36]. Currently, there is a wide variety of the experimental data which confirm different versions of these reactions mechanism: aziridinium imide (A), dipolar or biradical (B), and concerted (C) ones (Scheme 1). The A and B types result from the completion of the reaction under the addition of methanol molecules, used as the solvent or cosolvent in these reactions. In the case of reactions of active dienes with diethyl azodicarboxylate ($\mathbf{1}$) or 4-phenyl-1,2,4-triazoline-3,5-dione ($\mathbf{2}$), the major
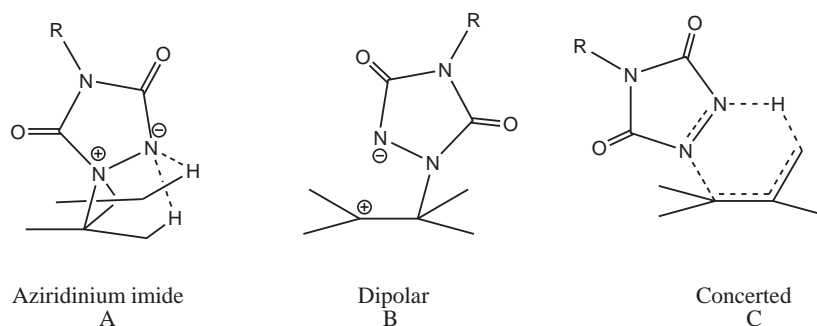
Scheme 1   Three versions of the ene reaction mechanism: aziridinium imide (A), dipolar or biradical (B), and concerted (C).

products are the [4+2]-cycloadducts with their stereospecificity preserved. In the case of less active dienes such as 1,3-cyclohexadiene [37] and Z,Z-1,4-disubstituted-1,3-butadienes [18,19,33], the ene reactions of **1** successfully compete with the DAR.

The series of 4-substituted-1,2,4-triazoline-3,5-diones has been studied with a number of dienes. All these dienophiles have the little difference in the reaction rates, which corresponds to the weak influence of 4-R substituents on the activity of the N=N reaction center [38,39].

The extensive study of the solvent influence on the rate of the DAR and ene reactions with **1** and **2** shows that the solvent polarity is not the main reason of reactivity changes [15,18,31–35,38–41]. Great similarity of the solvent influence in both DAR and ene-reactions with **1** ($R = 0.99$), as well as with **2** ($R = 0.99$) has been observed [40,41]. However, there is a large difference of the solvent effect on the reaction rates with **1** when compared with **2**.

In this paper, we discuss some possible reasons for the differences in the solvent, temperature, and high hydrostatic pressure influences on the rate of the acyclic and cyclic N=N and C=C reaction centers in the DAR and ene reactions (Scheme 2) on the basis of new experimental data.

EXPERIMENTAL

Materials

All chemicals were purchased (Aldrich) and were used without further purification, except of **2**. 4-Phenyl-1,2,4-triazoline-3,5-dione (**2**) was purified by sublimation at 100°C and 10 Pa, mp 165–170°C (decomp.), λ_{max} (ε) = 540 (248) in benzene; 527 (186) in dioxane; 540 nm (245) in toluene. Cyclopentadiene (**4**) was obtained by the cracking of the crystalline dimer and was repeatedly distilled before the measurements. The

solvents were purified by standard methods [42]. Almost quantitative yields of adducts **15**, **17**, **19**, and their structures were described previously [38,39,43].

Adduct **14**. ^{1}H NMR, "Bruker Avance," 400 MHz, DCCl$_3$, 25°C, δ, ppm: 1.26 (t, [3]J(H,H) = 7.1 Hz, 6H, 2CH$_3$), 1.71–1.73 (m, 2H, CH$_2$), 2.95 (m, 2H, 2CH), 4.18 (q, [3]J(H,H) = 7.1 Hz, 4H, 2CH$_2$), 6.42–6.55 (m, 2H, 2CH) [44]*. *Adduct* **16**: mp 153–154°C; MS (70 eV), m/z calcd. for M **16** + Na$^+$: 402.8; found: 403.0. ^{1}H NMR, 400 MHz, DCCl$_3$, 25°C, δ: 0.99 (t, [3]J(H,H) = 7.1 Hz, 6H, 2CH$_3$); 2.66 (s, 6H, 2CH$_3$); 3.86–3.94 (m, 4H, 2CH$_2$); 7.17–7.57 (m, 8H, aromatic). These data and the absence of N–H signal are in agreement with the reactions **1** + **4** → **14** and **1** + **5** → **16**.

Apparatus and Procedures

Kinetic Measurements.   At normal pressure the rate of reactions **1** + **4** → **14**, **1** + **5** → **16**, and **1** + **7** → **21** were determined by measuring the UV absorption of reagents equimolar solutions (3–5) × 10^{-2} M at 400–405 nm (spectrophotometer Hitachi-2900), where adducts **14**, **16**, and **21** are transparent. The rate of fast reactions **2** + **4** → **15** and **2** + **7** → **20** was measured by the stopped-flow method (RX 2000, the spectrophotometer Cary 50 Bio). A very fast reaction **2** + **4** → **15** [$k_2 = (1.6 \pm 0.35) \times 10^5$ L mol^{-1} s^{-1}] was measured by the change of **2** absorption in toluene, 24.5°C at 550 nm with equimolar concentrations of **2** and **4** (0.004 mol L^{-1}). The rate of reaction **2** + **7** → **20** was measured by the stopped-flow method in 1,2-dichloroethane at 23.5°C, $k_2 = 335 \pm 9$ L mol^{-1} s^{-1}, and in benzene at 23.5°C, $k_2 = 55.6 \pm 0.5$ L mol^{-1} s^{-1}, and at 40.1°C, 90.5 ± 1.3 L mol^{-1} s^{-1}.

The rate constants of reactions **1** + **4** → **14** and **1** + **5** → **16** under elevated pressure were measured in

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* The same structure of adduct **14** has been previously suggested on the basis of the adduct transformation into bicyclo[2.1.0]pentane.
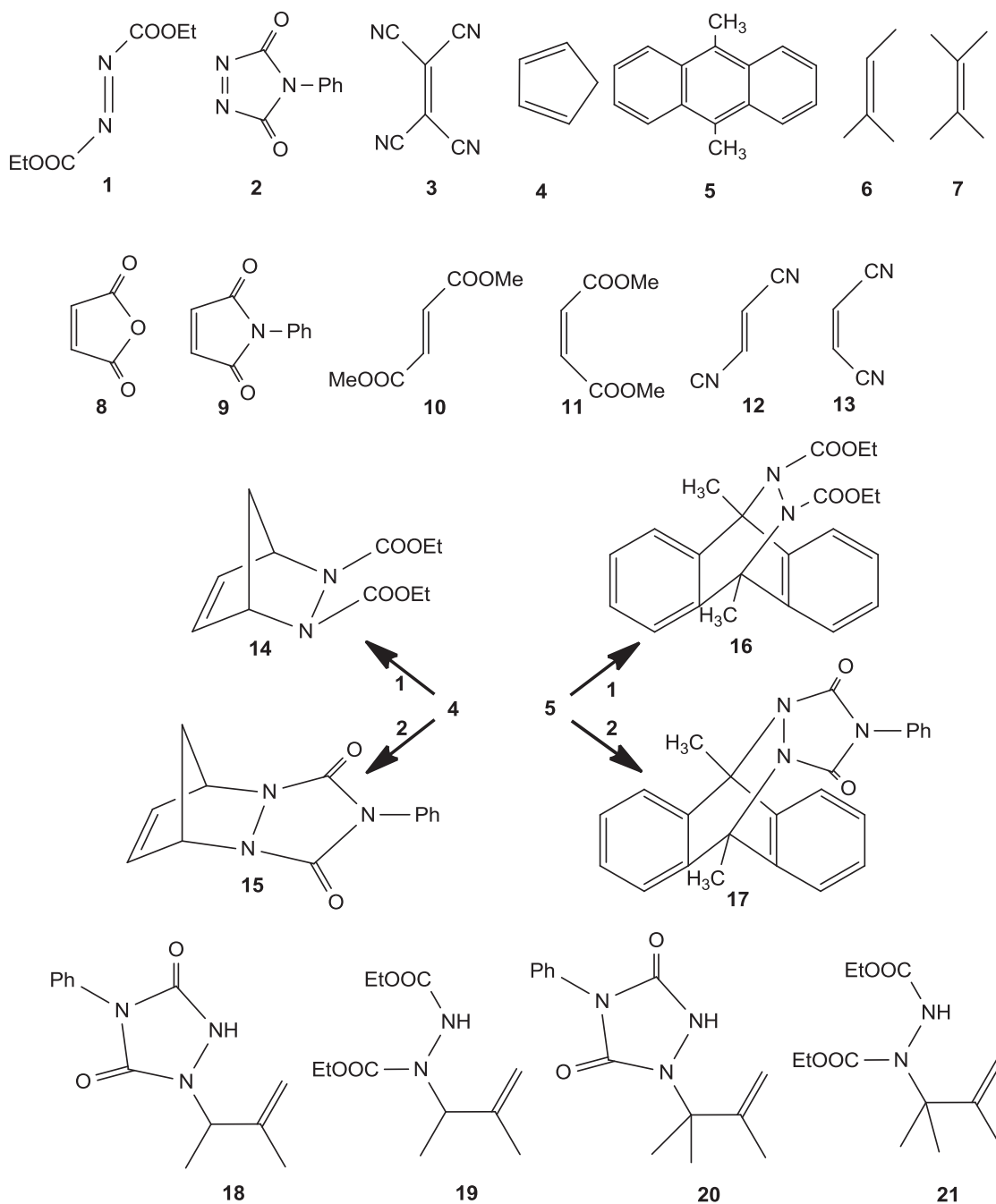
Scheme 2 Reagents with C=C and N=N reacting bonds in the DA and ene reactions.

a toluene solution at 25°C, using the high-pressure optical cell "PCI-500" produced by Syn (Japan), adjusted to the UV-spectrophotometer SCINCO.

Volume Parameters. The volumes of activation, $\Delta V^{\neq}$, were calculated using the dependence $\ln k_p$ vs. P, where

k_p is the rate constant of reactions $1 + 4 \rightarrow 14$ or $1 + 5 \rightarrow 16$ carried out under pressure P. It is important to compare the values of activation ($\Delta V^{\neq}$) and reaction ($\Delta_{r-n} V$) volumes, $\Delta V^{\neq} / \Delta_{r-n} V$. Here, we use the more accurate method of determination of $\Delta_{r-n} V$. As an example, for the reaction $1 + 4 \rightarrow 14$, the total volume of solution with reagents **1**, **4** and adduct **14** can be
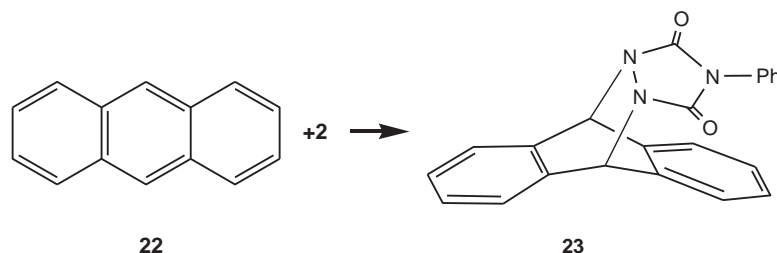
Scheme 3   The DA reaction of anthracene (**22**) with 4-phenyl-1,2,4-triazoline-3,5-dione (**2**) with adduct (**23**) formation.

expressed by Eqs. (1) and (2):

$$V_{(t)} = V_s + (c_{0,1} - c_{14,t}) \cdot V_1 + (c_{0,4} - c_{14,t}) \cdot V_4$$
$$+ c_{14,t} \cdot V_{14} \qquad (1)$$

$$V_{(t)} = [V_s + (c_{0,1} \cdot V_1 + c_{0,4} \cdot V_4)]$$
$$+ c_{14,t} \cdot (V_{14} - V_1 - V_4)$$
$$= V_{(t=0)} + c_{14,t} \cdot \Delta_{r-n} V \qquad (2)$$

$$1/d_{(t)} = 1/d_{(t=0)} + c_{14,t} \cdot \Delta_{r-n} V / 1000 d_{(t=0)} \quad (3)$$

Equation (3), derived from Eq. (2), is more convenient to measure the density of the reaction mixture. Here, $V_{(t=0)}$ and $V_{(t)}$ are the solution volumes at the beginning and during the reaction; V_s is the solvent volume; V_1, V_4, and V_{14} are the partial molar volumes of compounds **1**, **4**, and **14**; $c_{0,1}$, $c_{0,4}$, and $c_{14,t}$ are the initial molar concentrations of reagents **1** and **4**, and the current concentration of adduct **14**; $\Delta_{r-n} V$ is the reaction volume. The current concentration of adduct **14** can be calculated from the kinetic data or from the change of the optical density of the same solution in the densitometer and spectrophotometer. Linear dependences $1/d_{(t)}$ vs. c_{14} were observed for two measurements up to 95% conversion (Fig. 2). The vibration densimeter, model DSA 5000M, was employed to measure the solution density at 25 ± 0.002°C.

Calorimetric Experiment. The enthalpies of solution of compounds **2**, **22**, and **23** were measured at 25°C by the calorimetric method described previously [45]. The solid sample (30–50 mg) was added to the solvent (150 mL). Usually three to four consecutive dissolutions of each compound were carried out with the subsequent calibration of the calorimeter. The heat of reaction **1** + **4** → **14** was measured in 1,2-dichloroethane by the addition of **1** (40–60 mg) to the solution of **4** (150 mL, 0.1 M). The heat of the solution of **1** is

0.14 kJ mol^{-1}, and the heat of reaction **1** + **4**→**14** is –112.4 ± 3.3 kJ mol^{-1}. The heat of reaction of **2** + **4** → **15** is –134 ± 2 kJ mol^{-1} in benzene and –135 ± 2 kJ mol^{-1} in 1,2-dichloroethane solution.

Differences in the Solvation Enthalpies. The transfer of solvation enthalpies of reagents ($\partial_{tr} H_{(2+22)}$), adduct ($\partial_{tr} H_{(23)}$), and activated complex ($\partial_{tr} H_{AC}$) of the DA reaction **2** + **22**→**23** was calculated using benzene as the reference solvent [Eqs. (4)–(6)]:

$$\partial_{tr} H_{(2+22)} = (\Delta_{sol} H_{(2)} + \Delta_{sol} H_{(22)})_S$$
$$-(\Delta_{sol} H_{(2)} + \Delta_{sol} H_{(22)})_{benzene} \quad (4)$$

$$\partial_{tr} H_{(23)} = (\Delta_{sol} H_{(23)})_S - (\Delta_{sol} H_{(23)})_{benzene} \quad (5)$$

$$\partial_{tr} H_{AC} = \partial_{tr} H_{(2+22)} + \Delta H_S^{\#} - \Delta H_{benzene}^{\#} \quad (6)$$

Here, $\Delta_{sol} H_{(2)}$, $\Delta_{sol} H_{(22)}$, and $\Delta_{sol} H_{(23)}$ are the solution enthalpies of compounds **2**, **22**, and **23**, and $\Delta H^{\neq}$ is the enthalpy of activation of the reaction **2** + **22** → **23** in solvent (S) and in benzene.

RESULTS AND DISCUSSION

cis, trans-Dienophile Reactivity of N=N and C=C Bonds in the DA Reactions

4-Phenyl-1,2,4-triazoline-3,5-dione (**2**) is very active in the DAR with most of dienes [37–39,43,46]. For this reason, it is very convenient to study the heat of reactions, but is difficult to study the reaction rates at ambient and elevated pressure. Recently, the rates and reaction enthalpies of 15 dienes with **2** have been discussed [46]. The structure of the products of ene reactions between **2** and various alkenes and cycloalkenes was described [15,18,26–29,31–35,40,41,47]. A cis-Isomer of substance **1** is unknown. The reaction rates with **1** are usually very low. Useful information can be

Table I Rate Constant (k_2, L mol^{-1} s^{-1}) of the DA Reactions of Dienophiles (**1–3, 8–12**) with Cyclopentadiene (**4**) and with 9,10-Dimethylanthracene (**5**), and the Ene Reactions with Trimethylethylene (**6**) and with Tetramethylethylenes (**7**), the Ratio of Their Rates (k_i/k_j), and Enthalpies of Reactions in Solution ($\Delta_{r-n}H$, kJ mol^{-1}) at 25°C

Dienophile	Cyclopentadiene[a] (**4**)			9,10-Dimethylanthracene[a] (**5**)		
	k_2	k_i/k_j	$-\Delta_{r-n}H$	k_2	k_i/k_j	$-\Delta_{r-n}H$
trans-1,2- Dicyanoethylene (**12**)	8.1×10^{-4}	**12:13** = 0.89	126[b]	1.39×10^{-4}	**12:13** = 1.06	102[b]
cis-1,2- Dicyanoethylene (**13**)	9.1×10^{-4}		–	1.31×10^{-4}		–
Dimethyl fumarate (**10**)	7.4×10^{-4}	**10:11** = 120	–	6.70×10^{-6}	**10:11** = 1200	–
Dimethyl maleate (**11**)	6.3×10^{-6}		–	5.64×10^{-9}		–
Maleic anhydride (**8**)	5.56×10^{-2}	**8:10** = 7.5×10^3	129[b]	1.13×10^{-2}	**8:10** = 1.7×10^3	104[b]
N-Phenylmaleimide (**9**)	$7.05 \times 10^{-2\,b}$	**9:10** = 9.5×10^3	142[b]	$3.0 \times 10^{-2\,b}$	**9:10** = 4.5×10^3	117[b]
trans-Diethyl azodicar- boxylate (**1**)	$3.22 \times 10^{-2\,c}$	**2:9** = 2.3×10^6	112[c]	$1.57 \times 10^{-3\,c}$	**2:9** = 4.1×10^5	–
	$3.03 \times 10^{-3\,d}$	**4:5** = 2.7				
4-Phenyl-1,2,4-triazoline- 3,5-dione (**2**)	$1.6 \times 10^{5\,d}$	**2:1** = 5.2×10^7	134[c]	$1.22 \times 10^{4\,e}$	**2:1** = 7.8×10^6	118[e]
		4:5 = 13.1				
Tetracyanoethylene (**3**)	4.3×10^2	**2:3** = 370	113[b]	$9.3 \times 10^{4\,b}$	**2:3** = 0.13	88[b]
Enophile	**2-Methyl-2-butene (6)**			**2,3-Dimethyl-2-butene (7)**		
trans-Diethyl azodicar- boxylate (**1**)	9.15×10^{-5} (60°C)[f]	**7/6** = 0.4	–	6.25×10^{-6} /23.3°C)[c]		
		–		3.5×10^{-5} /60°C[c]		
4-Phenyl-1,2,4-triazoline- 3,5-dione (**2**)	8.3(24°C)[f]	**2:1** = 2.6×10^5	–	335(23.3°C)[g]	**2:1** = 5.3×10^7	150[c]
	24.3 (60°C)[f]	**7/6** = 40				

[a]From [11,49]. [b]From 48. [c]This work, in 1,2-dichloroethane. [d]This work, in toluene. [e]From 46. [f]From 41. [g]From 47.

obtained from the comparison of the kinetic parameters of the DAR of C=C and N=N reaction centers of dienophiles **1–3, 8–13** with cyclopentadiene (**4**) and 9,10- dimethylanthracene (**5**), as well as those of ene reactions with 2-methyl-2-butene (**6**) and 2,3-dimethyl-2-butene (**7**) (Scheme 2 and Table I).

Commonly a very high activity of **2** was attributed to its very high molecular π-acceptor properties. However, it was shown that the differences in the solvation energy of dienophiles **2** and **8** in π-donor solvents, such as chlorobenzene, benzene, toluene, *o*-xylene, are commensurate and significantly less as compared with that of the strong π-acceptor, tetracyanoethylene **3** [46]. This means that the π-acceptor properties of **2** and **8** are comparable and moderate. Therefore, increased by five to six orders of magnitude activity of **2** when compared with the structural analogue **9** was attributed to the reduced energy of the N=N π-bond, as compared with the C=C π-bond [46]. On the other hand, the acyclic N=N bond in **1** has very low activity. It is known that cyclopentadiene is less conjugated and the less π-donor diene compared with 9,10-dimethylanthracene [48]. Enhanced π-donor properties of 9,10-dimethylanthracene give the higher rate of reaction with such strong π-acceptors, as tetracyanoethylene. If the π-acceptor properties of dienophiles are weak, the stabilization energy is rather low and the activation barrier is largely controlled by the energy balance of the old bonds rupture and new bonds formation. Hence, in such systems the less conjugated cyclopentadiene should be a more active diene.

The substantial reduction of the activity of dimethyl maleate **11** as compared with the trans-isomer of **10** in the DAR with **4** ($k_{(10)}/k_{(11)} = 1.2 \times 10^2$) and with **5** ($k_{(10)}/k_{(11)} = 1.2 \times 10^3$) was observed [49]. This is the result of the steric hindrances of two ester groups of *cis*-dienophile **11**, what prevents the diene approach to the dienophile **11** from the both sides [11,49]. There are no such problems for trans-isomer **10**.

In the case of small-scale and rigid linear nitrile groups, such steric hindrance is not observed at all, and both dienophiles **12** and **13** have comparable rates (Table I). For cyclic planar molecules **8** and **9** both the increase in π-acceptor properties and the ring tension energy were observed [47,48]. The DAR rates of diene **4** with cyclic dienophiles of **8** and **9** increased

Table II   Rate Constants (k_2, L mol^{-1}s^{-1}), the Enthalpy ($\mathbf{\Delta H}^{\neq}$, kJ mol^{-1}), Entropy ($\mathbf{\Delta S}^{\neq}$, J mol^{-1}K^{-1}), and Free Energy ($\Delta G^{\neq}$, kJ mol^{-1}) Activation of the DAR $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$ in a Series of Solvents

Solvent	k_2 (15°C)	k_2 (25°C)	k_2 (30°C)	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	$\Delta G^{\neq}$
Toluene	0.00179	0.00303	0.00384	33.8 ± 0.2	180 ± 1	87.4 ± 0.2
Benzene	0.00279	0.00434	0.00563	30.6 ± 2.0	188 ± 6	86.6 ± 2.0
Acetonitrile	0.0191	0.0299	0.0353	27.6 ± 1.6	180 ± 5	81.2 ± 2.0
1,2-Dichloroethane	0.0230	0.0322	0.0386	22.4 ± 0.7	197 ± 2	81.1 ± 1.0
Trichloromethane	0.0739	0.0939	0.103	13.8 ± 0.6	217 ± 2	78.5 ± 1.0

significantly as compared to the sterically unstressed *trans*-dienophile **10**: $k_{(8)}/k_{(10)} = 7.5 \times 10^3$ and $k_{(9)}/k_{(10)} = 9.5 \times 10^3$. A similar ratio in the DAR with diene **5**, $k_{(8)}/k_{(10)} = 1.7 \times 10^3$ and $k_{(9)}/k_{(10)} = 4.5 \times 10^3$ was observed (Table I).

The replacement of the C=C bond in *N*-phenylmaleimide **9** by the N=N bond in 4-phenyl-1,2,4-triazoline-3,5-dione **2** leads to a further dramatic increase in the DAR rate: $k_{(2)}/k_{(9)} = 2.3 \times 10^6$ with **4** and $k_{(2)}/k_{(9)} = 4.1 \times 10^5$ with **5** (Table I).

In the DA reactions with C=C bonds, where diene is a π-donor and dienophile is a π-acceptor, the general proportionality between the changes of reagents orbital properties and charges at C=C reaction centers is usually observed [48]. Therefore, for a wide range of diene–dienophile systems with C=C reaction centers, simple dependences of the reaction rate on the donor–acceptor interaction energy and the DAR heat were obtained [48].

As it can be seen from Table I, the energy balance of the bonds rupture and formation (reaction enthalpy) for the DAR with structural analogues **2** and **9** is near the same. It means that the reactivity factors observed in the DAR with C=C bonds [48] cannot be valid for the DAR with N=N bonds.

The rate of reaction $\mathbf{2} + \mathbf{5} \rightarrow \mathbf{17}$ ($k_2 = 1.2 \times 10^4$ L mol^{-1}s^{-1}, toluene, 25°C, Table I) is sufficiently less than that of the reaction $\mathbf{2} + \mathbf{4} \rightarrow \mathbf{15}$ ($k_2 = (1.6 \pm 0.3) \times 10^5$ L mol^{-1}s^{-1}, toluene, 25°C, stopped-flow, this work). Similarly, **9** is more active in the DA reaction with **4** than with **5**. On the other hand, **2** is significantly more active than tetracyanoethylene **3** in the DAR with cyclopentadiene **4** ($k_2/k_3 = 370$), but less active in the reaction with the strong π-donor diene, 9,10-dimethylanthracene **5** ($k_2/k_3 = 0.13$, Table I). This is in agreement with the conclusion [46] that the π-acceptor properties of dienophiles **2** and **9** are both moderate in magnitude and considerably less than those of tetracyanoethylene **3**.

It is interesting to compare the activity of cyclic dienophiles **2** and **9** in the DAR with dienes **4** and **5**, and the activity of acyclic dienophiles **1** and **10**

with these dienes. The obtained kinetic data of reaction $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$ are given in Table II.

It should be pointed out once that the solvent influence on the rate of DAR $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$ (Table II) and on the reaction rate of **1** with 2,3-dimethylbutadiene [40] turned out to be proportional ($R = 0.99$). As it follows from Table II, highly negative entropy of activation is observed in all solutions. The contribution of entropy share, $T\Delta S^{\neq}$, to the value of free energy of activation is very large and equals 60–80%.

Activation and Reaction Volumes

Large negative values of the DAR activation entropy are often accompanied by the increased negative values of activation volume ($\Delta V^{\neq}$) [50,51]. The values of $\Delta V^{\neq}$ were determined from the dependence of the reaction rate constant upon the external pressure (Table III, Fig. 1).

Taking into account the solvent compressibility, the corrected value of the activation volume ($\Delta V^{\neq}{}_{\text{corr}}$) is calculated from Eq. (1) [51].

$$\Delta V^{\#}_{\text{corr}} - RT\, \partial \ln(k_P)/\partial P + (n-1)RT\beta_T \quad (7)$$

Table III   Pressure (P, bar) Influence on the Rate Constant (k_P, L mol^{-1}s^{-1}) of Reactions $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$ in Toluene and $\mathbf{1} + \mathbf{5} \rightarrow \mathbf{16}$ in 1,2-Dichloroethane at 25°C

Reaction $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$			Reaction $\mathbf{1} + \mathbf{5} \rightarrow \mathbf{16}$		
P	$10^3 \cdot k_P$	$\ln(k_P/k_{P=1})$	P	$10^3 \cdot k_P$	$\ln(k_P/k_{P=1})$
1	3.01	0	1	1.43	0
273	5.20	0.546	242	1.99	0.330
492	7.24	0.877	429	2.75	0.654
730	10.9	1.284	601	3.80	0.978
971	16.3	1.691	749	4.52	1.151
1256	25.3	2.130	991	6.68	1.541
1568	40.0	2.586	1285	10.0	1.945
			1567	13.1	2.218
			1930	22.2	2.742
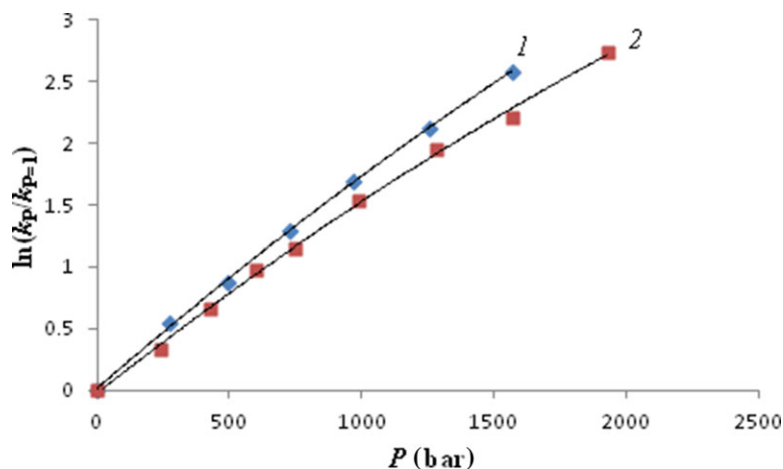
Figure 1 Pressure (P, bar) effect on the rate of reaction $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$ in toluene at 25°C (plot 1) and $\mathbf{1} + \mathbf{5} \rightarrow \mathbf{16}$ in 1,2-dichloroethane at 25°C (plot 2).

Here, β_T is the toluene compressibility (80.1×10^{-6} bar^{-1} [52]) and n is the reaction order. The experimental curve (Fig. 1) for the reaction $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$ is described by the polynomial equation (8):

$$\text{Ln}(k_p/k_{p=1}) = -0.000000141P^2 + 0.001860P;$$
$$R = 0.9998 \qquad (8)$$

Hence, for the DAR $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$, the experimental value of $\Delta V^{\neq}_{\text{exp}}$ is -46.0 ± 1.4 cm^3 mol^{-1} and the corrected one is -43.8 ± 1.4 cm^3 mol^{-1}. We also described the experimental data of this reaction by the logarithmic equation (9):

$$\text{Ln}(k_p/k_{p=1}) = 8.870\,\text{Ln}[(4633 + P)/4633];$$
$$R = 0.9987 \qquad (9)$$

From Eq. (9), it follows that the value of $\Delta V^{\neq}_{\text{exp}}$ is -47.4 ± 1.8 cm^3 mol^{-1} and $\Delta V^{\neq}_{\text{corr}}$ is -45.2 ± 1.8 cm^3 mol^{-1}.

For the DAR $\mathbf{1} + \mathbf{5} \rightarrow \mathbf{16}$, the experimental data (Table III, Fig. 1) were described by polynomial (10) and logarithmic (11) equations:

$$\text{Ln}(k_p/k_{p=1}) = -0.000000141P^2 + 0.0016944P;$$
$$R = 0.9992 \qquad (10)$$

$$\text{Ln}(k_p/k_{p=1}) = 8.798\,\text{Ln}[(5306 + P)/5306];$$
$$R = 0.9987 \qquad (11)$$

For the DAR $\mathbf{1} + \mathbf{5} \rightarrow \mathbf{16}$, the value of $\Delta V^{\neq}_{\text{exp}}$ is -42.0 ± 2.1 cm^3 mol^{-1} and $\Delta V^{\neq}_{\text{corr}}$ is -40.1 ± 2.1

cm^3 mol^{-1} from Eq. (10) and $\Delta V^{\neq}_{\text{exp}}$ is -41.0 ± 2.5 cm^3 mol^{-1} and $\Delta V^{\neq}_{\text{corr}}$ is -39.1 ± 2.5 cm^3 mol^{-1} from Eq. (11).

It should be noted that in accordance with the polynomial and logarithmic equations the values of the activation volumes at atmospheric pressure are close, which gives the average value of $\Delta V^{\neq}_{\text{corr}} = -44.5 \pm 1.8$ cm^3 mol^{-1} for the reaction $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$ and $\Delta V^{\neq}_{\text{corr}} = -39.6 \pm 2.5$ cm^3 mol^{-1} for the reaction $\mathbf{1} + \mathbf{5} \rightarrow \mathbf{16}$. However, polynomial equations, in contrast to logarithmic equations, imply the existence of the false peak at P 6.6 and 6.0 kbar, whereas Eqs. (9) and (11) can reliably determine the value of $\Delta V^{\neq}_{\text{exp}}$ and predict correctly the acceleration effect at elevated pressure.

It is useful to compare the values of activation ($\Delta V^{\neq}_{\text{corr}}$) and reaction ($\Delta_{r-n}V$) volumes. The value of $\Delta_{r-n}V$ was calculated from the dependence of the solution density during the reaction $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$ on the adduct $\mathbf{14}$ concentration (Fig. 2).

The average value of $\Delta_{r-n}V$ for the DA reaction $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$ is equal to -35.8 ± 0.3 cm^3 mol^{-1}. Similar measurements for the reaction $\mathbf{1} + \mathbf{5} \rightarrow \mathbf{16}$ gave the values of $\Delta_{r-n}V$: -21.8, -21.0, and -22.1 cm^3 mol^{-1} with the mean value -21.6 ± 0.4 cm^3 mol^{-1}. From the data obtained, it follows that the value of activation volume significantly exceeds the volume of the DAR $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{14}$, $\Delta V^{\neq}/\Delta_{r-n}V = -44.5/-35.8 = 1.24$, and even more for the DAR $\mathbf{1} + \mathbf{5} \rightarrow \mathbf{16}$, $\Delta V^{\neq}/\Delta_{r-n}V = -39.6/-21.6 = 1.83$. On the other hand, for the DAR with cyclic N=N $\mathbf{2}$ and C=C $\mathbf{9}$ bonds, the ratio $\Delta V^{\neq}/\Delta_{r-n}V$ differs insignificantly and is usually less or about unity. Thus, the reaction of $\mathbf{8} + \mathbf{5}$ in acetonitrile the ratio $\Delta V^{\neq}/\Delta_{r-n}V$ is $-20.0/-23.6 = 0.85$, and in the reaction of 9-phenylanthracene with $\mathbf{8}$ the ratio $\Delta V^{\neq}/\Delta_{r-n}V$
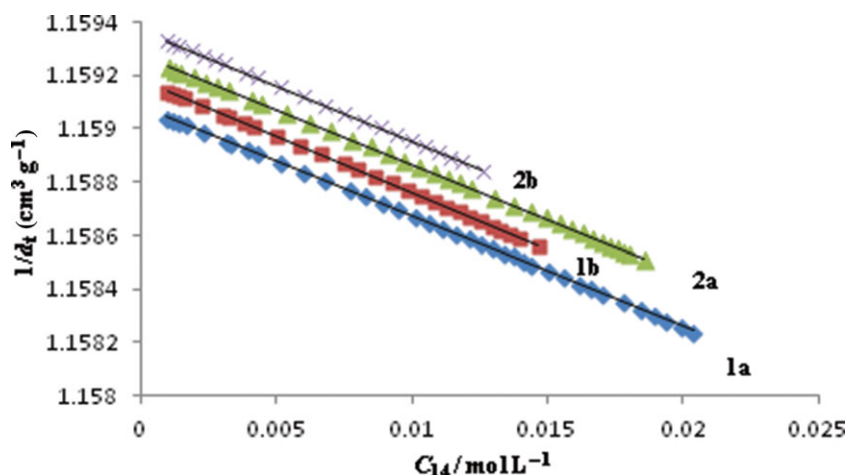
Figure 2   Relation between the specific volume ($1/d_t$, cm^3 g^{-1}) of the reaction $1+4 \rightarrow 14$ and the adduct concentration (c_{14}, mol L^{-1}) in toluene at 25°C. **1a**: $1/d_t = -0.04123\,c_{14} + 1.15908$; $R = 0.9999$; $c_{0,1} = 0.0221$ M; $c_{0,4} = 0.0625$ M; $\Delta_{r-n}V = -35.6 \pm 0.2$ cm^3 mol^{-1} (kinetic method). **1b**: $1/d_t = -0.04208c_{14} + 1.15918$; $R = 0.9999$; $c_{0,1} = 0.0221$ M; $c_{0,4} = 0.0625$ M; $\Delta_{r-n}V = -36.3 \pm 0.2$ cm^3 mol^{-1} (spectrophotometric method). For clarity, the values of d_t^{-1} of the line **1b** were displaced upward on 0.0001 of the ordinate scale. **2a**: $1/d_t = -0.04096\,c_{14} + 1.15927$; $R = 0.9999$; $c_{0,1} = 0.0203$ M; $c_{0,4} = 0.0717$ M; $\Delta_{r-n}V = -35.3 \pm 0.2$ cm^3 mol^{-1} (kinetic method). **2b**: $1/d_t = -0.04165\,c_{14} + 1.15937$; $R = 0.9999$; $c_{0,1} = 0.0203$ M; $c_{0,4} = 0.0717$ M; $\Delta_{r-n}V = -35.9 \pm 0.2$ cm^3 mol^{-1} (spectrophotometric method). For clarity, the values of d_t^{-1} of the line **2b** were displaced upward on 0.0001 of the ordinate scale.

is $-23.2/-27.3 = 0.84$ [51]. In the reaction of 9,10-diphenylanthracene with **2**, the ratio $\Delta V^{\neq}/\Delta_{r-n}V$ is $-17.2/-15.6 = 1.10 \pm 0.10$, and in the DAR of **2** with bicyclo[2.2.1]hepta-2,5-diene $\Delta V^{\neq}/\Delta_{r-n}V$ is $-25.1/-30.9 = 0.81 \pm 0.05$ [46]. The ratio $\Delta V^{\neq}/\Delta_{r-n}V$, close to unity, corresponds to near the same volume of the activated complex and reaction product.

Differences of the Solution Enthalpies in the DA Reaction $2 + 22 \rightarrow 23$

It is useful to compare the change of the solvation enthalpy transfer of reagents, activated complex, and adduct in a series of solvents. Necessary kinetic and calorimetric data for the DA reaction of anthracene **22** with **2** in 12 solvents are summarized in Table IV.

The analysis of the data in Table IV allows us to draw the following conclusions:

1. The change of the reaction rate ($\ln k_2$) is proportional to that of enthalpy ($\Delta H^{\neq}$, $R = 0.96$), entropy ($\Delta S^{\neq}$, $R = 0.98$) of activation, as well as to the reaction enthalpy ($\Delta_{r-n}H$, $R = 0.94$), solvation enthalpy transfer of dienophile **2** ($\partial_{sol}H_{(2)}$, $R = 0.94$), but not to that of diene **22** ($\partial_{sol}H_{(22)}$, $R = 0.12$).
2. Normalized empirical parameters of the solvent polarity (E_T^N) are in very poor correlations with the reaction rate ($\ln k_2$, $R = 0.15$) and solvation

enthalpy transfer of dienophile **2** ($\partial_{sol}H_{(2)}$, $R = 0.10$).
3. The change in the reaction rate in the solvents under study is mainly caused by the change in activation enthalpy ($\Delta\Delta H^{\neq} = 26.9$ kJ mol^{-1}; $T \cdot \Delta\Delta S^{\neq} = 14.9$ kJ mol^{-1}).
4. The change in reaction enthalpy ($\Delta_{r-n}H$) correlates poorly with the solvation enthalpy transfer of the reagents ($\partial_{tr}H_{(2+22)}$, $R = 0.81$) and the adduct ($\partial_{tr}H_{23}$, $R = 0.61$).
5. The solvation enthalpy transfer of the activated complex ($\partial_{tr}H_{AC}$) is determined neither by the enthalpy transfer of dienophile ($\partial_{tr}H_2$, $R = 0.16$) nor by that of both reagents ($\partial_{tr}H_{(22+2)}$, $R = 0.05$) and is weakly correlated with the enthalpy transfer of the adduct ($\partial_{tr}H_{23}$, $R = 0.80$).
6. The solvation enthalpy transfer of reagents ($\partial_{tr}H_{(22+2)}$) differs greatly from the enthalpy transfer of adduct ($\partial_{tr}H_{23}$, $R = 0.10$).
7. The value of solvation energy for the reagents (mainly of **2**) sharply decreases with the increase in the solvent acceptor number (AN) in contrast to the activated complex and adduct **23**.

As a result, we can conclude that nitrogen atoms in the N=N bond of dienophile **2** demonstrate electron–acceptor properties, but the N–N moiety in the

Table IV Enthalpies of Solution ($\Delta_{sol}H$, kJ mol^{-1}) of Anthracene (**22**), 4-Phenyl-1,2,4-triazoline-3,5-dione (**2**), Their Adduct (**23**), Enthalpy Transfer of Reagents ($\partial_{tr}H_{(2+22)}$), Activated Complex ($\partial_{tr}H_{AC}$) and Adduct ($\partial_{tr}H_{23}$) with Benzene as Blank, as well as the Rate Constants (k_2, L mol^{-1} s^{-1}), Enthalpies ($\Delta H^{\#}$, kJ mol^{-1}), Entropies ($\Delta S^{\#}$, J mol^{-1} K^{-1}) of Activation and Enthalpy of the DA Reaction ($\Delta_{r-n}H$, kJ mol^{-1}), Measured in 12 Solvents at 25°C

Solvent	k_2	$\ln k_2$	$\Delta H^{\#}$	$-\Delta S^{\#}$	$\Delta_{sol}H_{22}{}^a$	$\Delta_{sol}H_2{}^{b,c}$	$\Delta_{sol}H_{23}$	$\partial_{tr}H_{(2+22)}$	$\partial_{tr}H_{23}$	$\partial_{tr}H_{AC}$	$-\Delta_{r-n}H$	Acceptor Number^d	$(E_T^N)^d$
Tetrahydrofuran	0.028	-3.57	50.2	105	18.2	6.7	—	-20.4	—	-5.4	—	8.0	0.207
Ethyl acetate	0.057^b	-2.86	48.5^b	106^b	25.1	9.0	15.1	-11.2	-5.9	2.1	91.4	9.3	0.228
Methyl acetate	0.070	-2.66	46.4	113	25.0	9.9	—	-10.4	—	0.9	—	10.7	0.253
o-Xylene	0.21^c	-1.56	46.0	105	24.0	18.0	19.2	-3.3	-1.8	7.5	95.2	—	0.074
1,4-Dioxane	0.094^b	-2.36	43.9^b	117^b	22.6	8.8	14.1	-14.0	-6.9	-5.2	89.6	10.8	0.164
Toluene	0.33^c	-1.11	43.1	109	24.8	18.3	20.3	-2.3	-0.7	5.7	95.1	—	0.099
Benzonitrile	0.29	-1.24	41.8	117	25.6	13.6	—	-6.1	—	0.6	—	15.5	0.333
Acetonitrile	0.32	-1.14	38.5	125	28.0	14.2	15.6	-3.2	-5.4	0.1	98.9	18.9	0.460
Benzene	0.52^c 0.50^e	-0.67	35.2	134	24.7	20.6	21.0	(0)	(0)	(0)	96.7^f	8.2	0.111
Chlorobenzene	1.01^c	0.010	31.8	138	24.6	21.8	19.2	1.1	-1.8	-2.3	99.6	—	0.188
1,2-Dichloroethane	1.55	0.438	28.0	146	24.9	21.9	14.6	1.5	-6.4	-5.7	104.6	16.7	0.327
Trichloromethane	5.09	1.63	23.4	155	20.8	24.4	5.2	-0.1	-15.8	-11.8	112.4	23.1	0.259

^{a}From 53. ^{b}From 54. ^{c}From 55. ^{d}From 46. ^{e}From 39. ^{f}From calorimetric measurements of the reaction heat in benzene. Other data were calculated from relation: $\Delta_{r-n}H_S = \Delta_{r-n}H_{benzene} + \partial_{tr}H_{23} - \partial_{tr}H_{(2+22)}$.

Table V Rate Constant (k_2, L mol^{-1}s^{-1}) of the Ene Reaction of 1 with Tetramethylethylene 7, Enthalpy ($\Delta H^{\neq}$, kJ mol^{-1}) and Entropy ($\Delta S^{\neq}$, J mol^{-1}K^{-1}) Activation

Solvent	$10^5 \cdot k_2$ (T, °C)	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	$10^5 k_{(1+7)}/10^5 k_{(1+6)}{}^a$ at 60°C
Acetonitrile	0.323(25); 0.959(40); 1.74(50); 3.35(60)	52.3 ± 3.0	176 ± 10	3.35/7.6 = 0.43
1,2-Dichloroethane	0.682(25); 1.47(40); 2.19(50); 3.59(60)	36.4 ± 3.0	222 ± 10	3.59/9.15 = 0.40
Trichloromethane	1.26(25); 2.08(35); 2.58(40); 3.48(45); 4.07 (50); 6.4(60)	35.7 ± 3.0	219 ± 10	6.4/15.3 = 0.42

^{a}This work for the reaction $1 + 7 \rightarrow 21$ and data for the reaction $1 + 6 \rightarrow 19$ are obtained from 40.

activated complex and in reaction adduct **23** already has electron–donor properties.

Ene Reactions. Most of the 1,3-conjugated dienes in the absence of sterically hindrances react with azo-dienophiles **1** and **2**via concerted [4+2]-cycloaddition. When the s-cis-structure of 1,3-diene is distorted or un-available, the reaction can proceed as the ene-synthesis [26–36]. With the less active 1,3-dienes, the ene reactions of **2** and especially **1** may be preferable [26]. Many questions concerning the products structure, their regioselectivity, and the solvent influence on the rate of ene reactions have been considered [25–36]. In the ene reaction **8** with cyclohexene, the ratio $\Delta V^{\neq}/\Delta V_{r-n}$, –29.1/–25.0 is equal to 1.16 and in the ene reaction **2** with 1-hexene $\Delta V^{\neq}/\Delta V_{r-n}$ –31.0/–26.6 is also equal to 1.16 [47]. The data available showing the weak influence of the solvent polarity on the reaction rate allow us to exclude the solvent electrostriction in the solvation shell of the activated complex as the main cause resulting in the ratio, $\Delta V^{\neq}{}_{corr}/\Delta_{r-n}V >$ 1. Such an "abnormal" ratio ($\Delta V^{\neq}{}_{corr}/\Delta_{r-n}V > 1$) in the isopolar DA reactions was explained by different possibilities of solvent molecules to penetrate through the large steric hindered structures of the cyclic activated complex and cyclic adducts [13]. However, for these ene reactions an explanation of this ratio ($\Delta V^{\neq}{}_{corr}/\Delta_{r-n}V > 1$) can be given on the basis of the formation of more compact cyclic structure of the activated complex when compared to the noncyclical structure of reaction products. This assumption is in a good agreement with the previous investigations of the ene reactions of alkenes and enophiles with the C=O and C≡C reaction centers, where the ratio $\Delta V^{\neq}/\Delta_{r-n}V$ was in the range of 1.1–1.3 [50,56,57]. The activated complex should be more compact than the product of this ene reaction, as follows from the data of ab initio calculations ($\Delta V^{\neq}{}_W/\Delta V_{r-n,W} = 1.15$) [58,59].

It is important to emphasize that the analysis of regioselectivity of the ene reactions of **1** and **2** with substituted butenes allowed to discover the huge advantages of the primary attack on the less hindered C=C atom in alkenes with the higher charge stabilization on the double-substituted adjacent carbon atom [33–35,60,61].

Almost 100-fold unexpected decrease in the relative activity of **1** with the higher π-donor tetramethylethene compared with trimethylethene (Tables I and V) can probably be explained by the appearance of large steric hindrances that are more inherent to nonplanar molecule **1** than to the fixed planar molecule **2**.

SUMMARY

The highest reaction rates have been observed for 4-phenyl-1,2,4-triazoline-3,5-dione (**2**) in the DA reaction with cyclopentadiene **4** ($k_{2+4 \rightarrow 15} = 1.6 \times 10^5$ L mol^{-1} s^{-1}) and in the ene reaction of **2** with tetramethylethylene **7** ($k_{2+7 \rightarrow 20} = 335$ L mol^{-1} s^{-1}) for the first time. The ratio of the rate constants of the DA reaction of cyclopentadiene with **2** and with **1** in toluene at 25°C, $1.6 \times 10^5/3.03 \times 10^{-3} = 5.2 \times 10^7$, is very large and near the same as in the ene reactions of tetramethylethylene with **2** and with **1**, $335/6.25 \times 10^{-6} = 5.3 \times 10^7$.

Unusually high reactivity of the endocyclic N=N bond in **2** can be attributed to the increased electrophilicity of the N=N reaction center, as well as lower energy rupture of the π-N=N bond. From the analysis of the differences of solvation enthalpies in the DA reaction $2 + 22 \rightarrow 23$, it follows that the N=N bond in reagent **2** shows electron–acceptor properties; however, in the activated complex and in adduct **23**, the N–N moiety already shows electron–donor properties.

Comparison of the reactivity of the cyclic and acyclic dienophiles with C=C and N=N bonds (Table I) suggests that the DA reaction with 4-phenyl-1,2,4-triazoline-3,5-dione (**2**) proceeds more readily and easily than the ene reaction. For low activity of

diethylazocarboxylate (**1**), conversely, a stronger decrease in the activity is observed in the DA reaction, compared with the ene reaction. From the values of the enthalpies of these reactions, it can be concluded that these reactions are irreversible.

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