Received: 26 January 2018 | Revised: 14 May 2018

DOI: 10.1002/kin.21189

Kinetics of the ene reactions of 4-phenyl-1,2,4-triazoline-3,5-dione with β-pinene and 2-carene: Temperature, high pressure, and solvent effects

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Abstract

The data on temperature, solvent, and high hydrostatic pressure influence on the rate of the ene reactions of 4-phenyl-1,2,4-triazoline-3,5-dione (**1**) with 2-carene (**2**), and β-pinene (**4**) have been obtained. Ene reactions **1+2** and **1+4** have high heat effects: $\Delta H_{r\text{-}n}$ (**1+2**) −158.4, $\Delta H_{r\text{-}n}$(**1+4**) −159.2 kJ mol^{-1}, 25°C, 1,2-dichloroethane. The comparison of the activation volume ($\Delta V^{\neq}$(**1+2**) −29.9 cm^3 mol^{-1}, toluene; $\Delta V^{\neq}$(**1+4**) −36.0 cm^3 mol^{-1}, ethyl acetate) and reaction volume values ($\Delta V_{r\text{-}n}$(**1+2**) −24.0 cm^3 mol^{-1}, toluene; $\Delta V_{r\text{-}n}$(**1+4**) −30.4 cm^3 mol^{-1}, ethyl acetate) reveals more compact cyclic transition states in comparison with the acyclic reaction products **3** and **5**. In the series of nine solvents, the reaction rate of **1+2** increases 260-fold and **1+4** increases 200-fold, respectively, but not due to the solvent polarity.

KEYWORDS

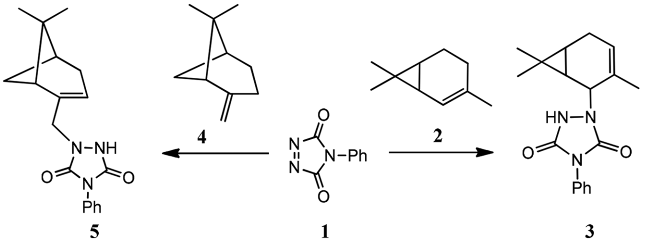
activation volume, high pressure, kinetics, reaction heat, reaction volume

1 | INTRODUCTION

4-Phenyl-1,2,4-triazoline-3,5-dione (**1**) contains a very active N=N bond and easily enters ene reactions with substrates containing an allylic hydrogen atom.[1–5] These reactions are of both synthetic [1,4] and mechanistic interest.[2,4–7] An extensive use of **1** in organic synthesis caused by its ability to be involved in a large number of easily running quantitative and selective reactions with a wide variety of active and low-active substrates.[1,4,8–16] Reagent **1** shows increased activity in [4+2]-, [2+2]-cycloaddition and ene reactions compared to other dienophiles, including the strongest π-acceptor dienophile, tetracyanoethylene.[2,16–21]

It has been proven that 2-carene (**2**) and β-pinene (**4**) enter ene reactions with **1** to form adducts **3** and **5**, respectively.[22] However, there were no quantitative data dealing with the kinetics of these reactions.

In this work, we determined the rate constants of the reactions **1+2** → **3** and **1+4** → **5** in nine solvents at 20, 30, and 40°C as well as the enthalpies of these reactions. We also studied the pressure influence on these reactions rates, calculated the values of activation and reaction volumes, and compared the data obtained with the parameters of a number of other reactions involving **1**.



2 | EXPERIMENTAL

2.1 | Materials

2-Carene ((1*S*,6*R*)-3,7,7-trimethylbicyclo[4.1.0]hept-2-ene) (**2**) (Sigma-Aldrich, 97%, Switzerland) and β-pinene (6,6-

dimethyl-2-methylenebicyclo[3.1.1]heptane) (**4**) (Sigma-Aldrich, 99%, USA, MO) were used without further purification. 4-phenyl-1,2,4-triazoline-3,5-dione (Sigma-Aldrich, 97%, USA, MO) was sublimated at 100°C and 100 Pa before the measurements. The m.p. of **1** is 165-170°C, decomp.[18] The purity of **1** was tested according to the known absorption coefficients.[16] The ^1H and ^{13}C NMR spectra of the obtained adducts **3** and **5** completely coincide with the spectra given earlier.[22] All solvents were purified by known methods.[23]

2.2 | Kinetic measurements at ambient pressure

The reaction rate was monitored with the UV spectrophotometer (Hitachi U-2900, Japan) according to a change in the absorption of **1** (530-550 nm). The temperature of the working solution in a quartz cuvette with a ground glass stopper was maintained with an accuracy of ±0.1°C. The stability of reagent **1** in all the studied solvents was checked by stability of its absorption during the reaction time. The inaccuracies of the rate constants were ±3%, the enthalpy of activation ± 2 kJ mol^{-1}, and activation entropy ±6 J mol^{-1} K^{-1}.

2.3 | Kinetic measurements at elevated hydrostatic pressure

The pressure effect on the rate of the reactions **1+2** → **3** (toluene) and **1+4** → **5** (ethyl acetate) was studied at 25°C with the usage of a pressure multiplier (HP-500, Japan), a quartz cell with the variable volume (PCI-500, Japan) and UV spectrophotometer (SCINCO S-3100, Korea). The observed activation volume ($\Delta V^{\neq}_{exp}$; Equation 2) of the reactions **1+2** → **3** and **1+4** → **5** was calculated on the basis of the rate constants measured at 1 and 1000 bar, applying the previously proposed[24] relationship 1. Kinetics of the reactions **1+2** → **3** and **1+4** → **5** was studied in various solvents to optimize monitoring conditions:

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T,P=1} = (1.15 \pm 0.03) \times 10^{-3} \cdot \ln\left(\frac{k_{P=1000}}{k_{P=1}}\right) \quad (1)$$

$$\Delta V^{\neq}_{\text{exp}} = -RT\left(\frac{\partial \ln k}{\partial P}\right)_T \quad (2)$$

Corrected values of activation volumes ($\Delta V^{\neq}_{corr}$) of the reactions **1+2** → **3** and **1+4** → **5** were determined by Equation 3, taking into account isothermal compressibility coefficients of toluene, β_T 9.19 × 10^{-5} bar^{-1}, and ethyl acetate, β_T 1.20 × 10^{-4} bar^{-1}, respectively:[25]

$$\Delta V^{\neq}_{\text{corr}} = \Delta V^{\neq}_{\text{exp}} + \beta_T RT \quad (3)$$

2.4 | Reaction volumes

The reaction volume of the reaction **1+2** → **3** was determined by the kinetic method.[26] This method uses the dependence of the reaction mixture density on the concentration of the adduct (Equation 4):

$$\frac{1}{d_{(t)}} = \frac{1}{d_{(t=0)}} + \frac{C_{\text{add}(t)} \cdot \Delta V_{r-n}}{1000 \cdot d_{(t=0)}} \quad (4)$$

Here $d_{(t=0)}$ and $d_{(t)}$ are the densities of solution at the beginning and during reaction; $C_{\text{add},(t)}$ is the current concentration of adduct, calculated from kinetic data. The density of reaction mixtures was determined using a precision (±2 × 10^{-6} g cm^{-3}) densitometer (DSA 5000 M, Anton Paar, Austria) at 25 ± 0.002°C.

The volume of the reaction **1+4** → **5** was determined in two ways: by the kinetic method [26] and from the difference of the partial molar volumes (Equation 5):

$$\Delta V_{r-n} = V_5 - V_4 - V_1 \quad (5)$$

Here V_1, V_4, and V_5 are the partial molar volumes of compounds **1**, **4**, and **5**, respectively.

2.5 | Calorimetric measurements

The enthalpies of the reactions **1+2** → **3** and **1+4** → **5** were determined in 1,2-dichloroethane at 25°C with the employment of the differential calorimeter. The protocol of measurement was described earlier.[16,17] A sample of the crystals **1** was introduced into each of the solutions of bicyclic monoterpenes, **2** or **4** taken in excess. Three consecutive measurements were made for each reaction, **1+2** → **3** and **1+4** → **5**. The values of reaction enthalpy were calculated taking into account the heat of solution of crystals **1** in 1,2-dichloroethane, 21.9 kJ mol^{-1}.

3 | RESULTS AND DISCUSSION

The kinetic data and the activation parameters obtained of the reactions **1+2** → **3** and **1+4** → **5** in nine solvents are collected in Table 1.

It should be noted that the rates of the reactions **1+2** → **3** and **1+4** → **5** in such polar solvents as dimethylformamide and acetonitrile is noticeably less than in low polar solvents. The activation entropy of the reactions **1+2** → **3** and **1+4** → **5** closely corresponds to the activation entropy of other reactions of ene synthesis as well as the [4+2]-, [$2\pi+2\sigma+2\sigma$]-, [$2\pi+2\pi+2\pi$]-cycloaddition, but is significantly less in magnitude than that of the [$2\pi+2\pi$]-cycloaddition reaction (Table 2).

In the reaction **1+9** the C=C bond shifting to the nodal atom of bicycle **9** is forbidden by the Bredt rule. However, the

TABLE 1 The rate constants (k_2/L mol^{-1} s^{-1}) of the reactions **1**+**2** → **3** and **1**+**4** → **5** in the temperature range 20–40°C in a series of solvents with different permittivity (ε), enthalpy ($\Delta H^{\neq}$/kJ mol^{-1}), entropy ($\Delta S^{\neq}$/J mol^{-1} K^{-1}), and Gibbs free energy ($\Delta G^{\neq}$/kJ mol^{-1}) of activation

		1+2 → 3						**1+4 → 5**					
Solvent	**ε (25 °C)** [a]	**k_2 (20°C)**	**k_2 (30°C)**	**k_2 (40°C)**	**$\Delta H^{\neq}$**	**$-\Delta S^{\neq}$**	**$\Delta G^{\neq}$ (20°C)**	**k_2 (20°C)**	**k_2 (30°C)**	**k_2 (40°C)**	**$\Delta H^{\neq}$**	**$-\Delta S^{\neq}$**	**$\Delta G^{\neq}$ (20°C)**
N,N-Dimethylformamide	36.7	0.0172	0.0337	0.0623	46.7	119	81.6	0.0347	0.0667	0.1226	45.7	117	80.0
2-Propanone	20.6	0.0247	0.0477	0.0827	43.3	128	80.8	0.0506	0.0912	0.153	39.8	134	79.1
Ethyl acetate	6.0	0.0215	0.0407	0.0690	42.1	133	81.1	0.0518	0.0941	0.156	39.6	134	78.9
1,4-Dioxane	2.2	0.0438	0.0744	0.121	38.8	139	79.5	0.0990	0.177	0.266	35.3	144	77.5
Acetonitrile	35.9	0.172	0.296	0.432	32.6	148	76.0	0.256	0.423	0.637	32.4	146	75.2
Toluene	2.4	0.162	0.276	0.405	32.4	149	76.1	0.374	0.606	0.945	32.9	141	74.2
Benzene	2.3	0.238	0.388	0.574	31.2	151	75.5	0.563	0.917	1.36	31.3	143	73.2
1,2-Dichloroethane	10.4	1.39	1.93	2.58	21.5	170	71.3	2.44	3.38	4.64	22.2	161	69.4
Chloroform	4.6	4.45	–	–	–	–	68.0	7.55	10.0	–	20.7	157	66.7

[a] The values of permittivity are taken from Ref. 23.

reaction of the [2π+2π]-cycloaddition has turned out to be less advantageous in comparison with the Wagner-Meerwein rearrangement.[14,20] The increased activity of **1**, even with regard to tetracyanoethylene, as well as the increased stability of adducts in all reactions with **1** (Table 2) allowed us to carry out the [4+2]-cycloaddition reaction of **1** with 9,10-diphenylanthracene (**13**), where the active 9,10-reaction centers of **13** are sterically inaccessible. Nevertheless, the reaction **1+13** easily proceeds on the available 1,4-diene atoms of **13**.[30,31]

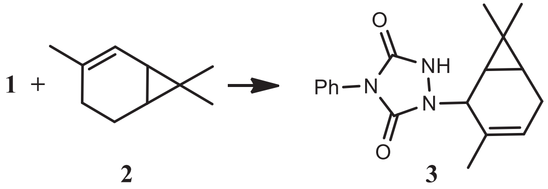
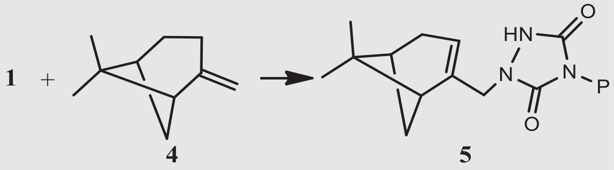
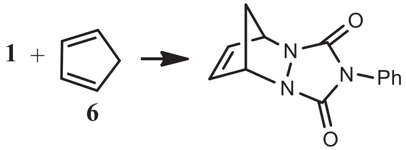
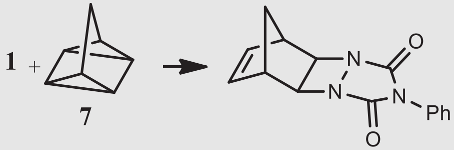
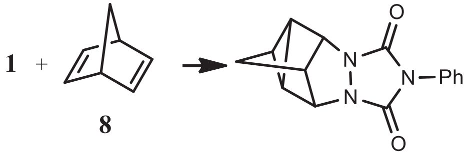
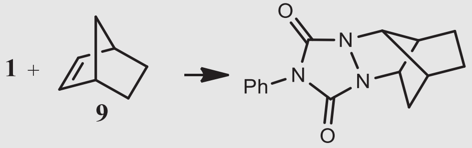
The energy balance between breaking and formation of the bonds reflected in the reaction enthalpy is minimal in the reactions **1+10** and **1+13** and is maximal for the reaction with nonconjugated norbornadiene, **1+8**, and also for the reaction involving two cyclopropane rings of quadricyclane, **1+7**. However, according to the data presented (Table 2), it follows that the high exothermicity of the reaction rarely determines the reaction rate.

The enthalpies of the reactions **1+2** → **3** and **1+4** → **5** were determined in 1,2-dichloroethane at 25°C from the data of three consistent dissolutions of crystals **1** in the solutions of **2** and **4**, respectively. Taking into account the heat of dissolution of **1** in 1,2-dichloroethane (21.9 kJ mol^{-1}) for the reaction **1+2** → **3,** the value of $\Delta \bar{H}_{r-n}$ is −158.4 ± 0.9 kJ mol^{-1} (−157.3, −159.7, and −158.2 kJ mol^{-1}), and for the reaction of **1+4** → **5** this value is −159.1 ± 1.1 kJ mol^{-1} (−157.5, −160.5, and −159.4 kJ mol^{-1}). High exothermicity of these **1+2** → **3** and **1+4** → **5** reactions allows us to consider them practically irreversible. It can be noted that these values of enthalpies of the **1+2** → **3** and **1+4** → **5** reactions are very close to that of the reaction of **1** with cyclohexene (ΔH_{r-n} −155.9 ± 0.4 kJ mol^{-1}, toluene, 25°C [Ref. 13]).

The activation volume for the reaction **1+2** → **3** has been determined in toluene at 25°C according to the data on the reaction rate at atmospheric (1 bar) and elevated (1000 bar) pressure (Equations 1–3). From the obtained ratio $k_{P\,=\,1000}/k_{P\,=\,1}$ equal to 3.10, the observed value $\Delta V^{\neq}_{\text{exp}}$ = −32.2 ± 1.0 cm^3 mol^{-1} has been calculated. Taking into account the change in the reagents concentration due to the solvent compressibility, the corrected activation volume ($\Delta V^{\neq}_{\text{corr}}$) is −29.9 ± 1.0 cm^3 mol^{-1} ($\beta_T RT$ = 2.3 cm^3 mol^{-1}). The activation volume ($\Delta V^{\neq}_{\text{corr}}$) for the reaction **1+4** → **5** in ethyl acetate is equaled −36.0 ± 1.5 cm^3 mol^{-1} ($k_{P\,=\,1000}/k_{P\,=\,1}$ = 3.92, $\Delta V^{\neq}_{\text{exp.}}$ = −39.0 ± 1.0 cm^3 mol^{-1}, $\beta_T RT$ = 3.0 cm^3 mol^{-1}). The difference in the values of the activation volume of these reactions ($\Delta\Delta V$ = 6.1 cm^3 mol^{-1}) can be explained by the solvent influence: For the reaction of bisadamantylidene **10** with **1**, the activation volume $\Delta V_{\text{corr}}{}^{\neq}$ is −50.8 ± 1.4 cm^3 mol^{-1} in toluene, and −55.8 ± 1.5 cm^3 mol^{-1} in ethyl acetate, that is the difference in activation volumes is equal to 5.0 cm^3 mol^{-1}.[29] It can be noted that the activation volumes of the reactions of **1+2** → **3** ($\Delta V^{\neq}_{\text{corr}}$ = −29.9 ± 1.0 cm^3 mol^{-1}, toluene) and of **1** with cyclohexene ($\Delta V^{\neq}_{\text{corr}}$ = −29.1 ± 0.5 cm^3 mol^{-1}, toluene, 25°C [Ref. 13]) coincide within the limits of measurement inaccuracies. To determine the reaction volume ($\Delta V_{r\text{-}n}$) of **1+2** → **3**, two cycles of measurements (Equations 6 and 7) were carried out. The volume of reaction **1+4** → **5** was determined by the kinetic method (Equations 8 and 9) and by the difference of the partial molar volumes of the adduct and reagents in ethyl acetate (Equation 10):

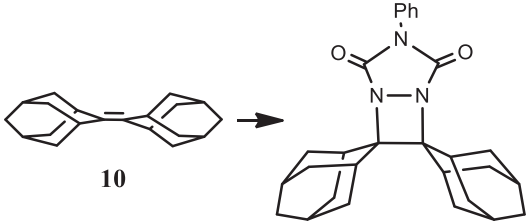
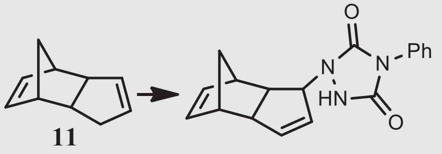
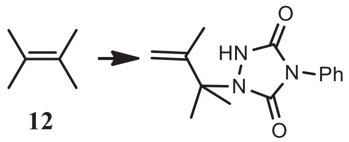
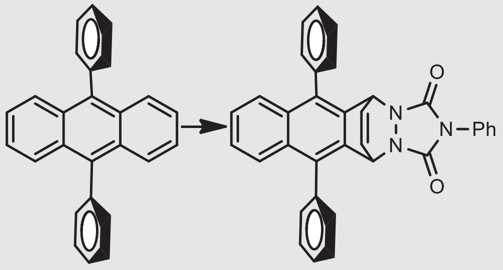
$$\begin{aligned} d^{-1} &= -(0.0278995 \pm 0.000126) \cdot c_3 \\ &\quad + (1.1594608 \pm 0.0000004);\ R^2 = 0.9996 \\ \Delta V_{1+2\to 3} &= -24.1\ \text{cm}^3\text{mol}^{-1};\ c_{01} = 5.06 \times 10^{-3}\text{mol}\ L^{-1}, \\ &\quad c_{02} = 5.50 \times 10^{-3}\text{mol}\ L^{-1} \end{aligned} \tag{6}$$

TABLE 2 The rate constants (k_2/L mol^{-1} s^{-1}), enthalpies ($\Delta H^{\neq}$/kJ mol^{-1}), entropies ($\Delta S^{\neq}$/J mol^{-1} K^{-1}), activation volumes ($\Delta V^{\neq}$/cm^3 mol^{-1}), reaction volumes ($\Delta V_{r\text{-}n}$/cm^3 mol^{-1}), and enthalpies ($\Delta H_{r\text{-}n}$ /kJ mol^{-1}) of a series of reactions involving 4-phenyl-1,2,4-triazoline-3,5-dione 1 in various solvents at 25°C

Reaction	Reaction type	k_2	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	$-\Delta V^{\neq}/-\Delta V_{r\text{-}n}$	$-\Delta H_{r\text{-}n}$
Reaction  	Ene	0.210 S-1	32.4 S-1	149 S-1	29.9/24.0 S-1	158.4 S-2
 	Ene	0.070 S-3	39.8 S-3	134 S-3	36.0/30.4 S-3	159.2 S-2
 	[$4\pi+2\pi$]	1.6×10^5 S-1 [Ref. 16]	–	–	–	134 S-4 [Ref. 16]
 	[$2\pi+2\sigma+2\sigma$]	0.282 S-1 [Ref. 27]	39.6 S-1 [Ref. 27]	123 S-1 [Ref. 27]	25.4/20.9 S-1 [Ref. 27]	255 S-1 [Ref. 27]
 	[$2\pi+2\pi+2\pi$]	3.95×10^{-3} S-1 [Ref. 28]	50.9 S-1 [Ref. 28]	121 S-1 [Ref. 28]	25.1/30.9 S-1 [Ref. 28]	218 S-1 [Ref. 28]
 	Ene with the Wagner-Meerwein rearrangement	1.28×10^{-4} S-1 [Ref. 14]	55.3 S-1 [Ref. 14]	134 S-1 [Ref. 14]	26.6/24.6 S-1 [Ref. 14]	170 S-2 [Ref. 14]

(Continues)

TABLE 2 (Continued)

Reaction	Reaction type	k_2	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	$-\Delta V^{\neq}/-\Delta V_{r\text{-}n}$	$-\Delta H_{r\text{-}n}$
1 +  **10**	[2π+2π]	0.0175 S-1 [Ref. 29]	24 S-1 [Ref. 29]	198 S-1 [Ref. 29]	50.8/37.6 S-1 [Ref. 29]	86.3 S-2 [Ref. 29]
1 +  **11**	Ene	0.0171 S-1 [Ref. 15]	46 S-1 [Ref. 15]	125 S-1 [Ref. 15]	27.6/20.6 S-1 [Ref. 15]	172 S-2 [Ref. 15]
1 +  **12**	Ene	55.6 S-4 (23.3℃) [Ref. 13]	20 S-4 [Ref. 13]	144 S-4 [Ref. 13]	–	150 S-2 [Ref. 13]
1 +  **13**	[4π+2π]	2.74×10^{-3} S-1 [Refs. 30,31]	58.6 S-1 [Refs. 30,31]	97 S-1 [Refs. 30,31]	17.5/15.4 S-1 [Refs. 30,31]	50.2 S-1 [Refs. 30,31]

[a] Solvents: S-1, toluene; S-2, 1,2-dichloroethane; S-3, ethyl acetate; S-4, benzene.

$$
\begin{aligned}
d^{-1} &= -(0.0277264 \pm 0.000180) \cdot c_3 \\
&\quad + (1.1593645 \pm 0.0000006);\ R^2 = 0.9992 \\
\Delta V_{\mathbf{1+2}\to\mathbf{3}} &= -23.9\ \mathrm{cm^3\ mol^{-1}};\ c_{01} = 5.06 \times 10^{-3}\,\mathrm{mol\,L^{-1}}, \\
&\quad c_{01} = 5.50 \times 10^{-3}\,\mathrm{mol\,L^{-1}}. \\
\Delta V_{\mathbf{1+2}\to\mathbf{3}} &= -24.0 \pm 0.1\ \mathrm{cm^3\ mol^{-1}}
\end{aligned} \tag{7}
$$

$$
\begin{aligned}
d^{-1} &= -(0.0346118 \pm 0.00039) \cdot c_5 \\
&\quad + (1.1178038 \pm 0.00000087);\ R^2 = 0.9979 \\
\Delta V_{\mathbf{1+4}\to\mathbf{5}} &= -30.9 \pm 0.5\mathrm{cm^3\ mol^{-1}}; \\
&\quad c_{01} = c_{04} = 5.00 \times 10^{-3}\,\mathrm{mol\,L^{-1}}
\end{aligned} \tag{8}
$$

$$
\begin{aligned}
d^{-1} &= -(0.0331679 \pm 0.000279) \cdot c_5 \\
&\quad + (1.1177995 \pm 0.00000066);\ R^2 = 0.9985 \\
\Delta V_{1+4\to5} &= -29.8 \pm 0.3\ \mathrm{cm^3\ mol^{-1}}; \\
&\quad c_{01} = c_{02} = 5.00 \times 10^{-3}\,\mathrm{mol\,L^{-1}}. \\
\Delta V_{1+4\to5} &= -30.4 \pm 0.5\ \mathrm{cm^3\ mol^{-1}}
\end{aligned} \tag{9}
$$

$$
\begin{aligned}
\Delta V_{\mathbf{1+4}\to\mathbf{5}} &= V_5 - V_1 - V_4 = 257.2 - 129.0 - 158.8 \\
&= -30.6 \pm 1.0\ \mathrm{cm^3\ mol^{-1}}
\end{aligned} \tag{10}
$$

Both methods give identical values of the reaction volume of **1**+**4** → **5**. The ratio of activation and reaction volumes ($\Delta V^{\neq}_{\mathrm{corr}}/\Delta V_{r\text{-}n}$) for the reaction of **1**+**2** → **3** is 1.25, and for **1**+**4** → **5** is 1.18. Note that for all ene reactions under the study the ratio $\Delta V^{\neq}_{\mathrm{corr}}/\Delta V_{r\text{-}n}$ is always more than one.[13–17] Solvent electrostriction for the activated complex can be excluded from consideration due to small and irregular solvent effect on the reaction rates. These ratios can be explained by the cyclic and, therefore, more compact form of the activated complex as compared with the acyclic form of the reaction adduct. This conclusion agrees with the results of the study of ene reactions of alkenes with enophiles containing C=O and C≡C reaction centers,[32–34] where the value of $\Delta V^{\neq}_{\mathrm{corr}}/\Delta V_{r\text{-}n}$ was in the range 1.1-1.3.

In the series of solvents (Table 1), the reaction rates of the **1**+**2** → **3** and **1**+**4** → **5** differ by two orders of magnitude; however, these changes take place not due to the solvent polarity. Similar activation of dienophiles in *H*-donor solvents is well known for other types of reactions. Previously, the solvent effect on the rate of the number of reactions involving dienophile **1** has been considered, which makes it possible to compare the solvent effect on the rate of the studied ene reactions **1**+**2** → **3** and **1**+**4** → **5** with regard to the [2π+2σ+2σ]-cycloaddition reaction of **1** with quadricyclane (**7**),[27] ene reaction with 2-methylbutene-2 (**14**),[35] [2π+2π]-cycloaddition reaction of **1** with 2-chloroethylvinyl ether (**15**),[36] ene reaction between **1** and norbornene (**9**) [14,20] with Wagner-Meerwein rearrangement, ene reaction of **1** with *trans*-hexene-3 (**16**),[21] [4π+2π]-cycloaddition reaction of **1** with anthracene (**17**),[17] and [2π+2π]-cycloaddition reaction of **1** with bisadamantylidene (**10**)[29] (Equations 11–18):

$$
\ln k\,(\mathbf{1}+\mathbf{2}) = (1.04 \pm 0.03) \cdot \ln k\,(\mathbf{1}+\mathbf{4}) - (0.65 \pm 0.07);\quad R^2 = 0.9939,\ N = 9 \tag{11}
$$

$$
\ln k\,(\mathbf{1}+\mathbf{7}) = (0.82 \pm 0.14) \cdot \ln k\,(\mathbf{1}+\mathbf{4}) + (0.13 \pm 0.29);\quad R^2 = 0.8515,\ N = 8 \tag{12}
$$

$$
\ln k\,(\mathbf{1}+\mathbf{15}) = (0.52 \pm 0.03) \cdot \ln k\,(\mathbf{1}+\mathbf{4}) + (2.65 \pm 0.08);\quad R^2 = 0.9869,\ N = 5 \tag{13}
$$

$$
\ln k\,(\mathbf{1}+\mathbf{9}) = (0.46 \pm 0.01) \cdot \ln k\,(\mathbf{1}+\mathbf{4}) - (6.73 \pm 0.01);\quad R^2 = 0.9995,\ N = 4 \tag{14}
$$

$$
\ln k\,(\mathbf{1}+\mathbf{16}) = (0.88 \pm 0.18) \cdot \ln k\,(\mathbf{1}+\mathbf{4}) - (2.55 \pm 0.35);\quad R^2 = 0.9588,\ N = 3 \tag{15}
$$

$$
\ln k\,(\mathbf{1}+\mathbf{17}) = (0.88 \pm 0.04) \cdot \ln k\,(\mathbf{1}+\mathbf{4}) - (0.20 \pm 0.06);\quad R^2 = 0.9919,\ N = 7 \tag{16}
$$

$$
\begin{aligned}
\ln k\,(\mathbf{1}+\mathbf{10}) &= (1.0730 \pm 0.2603) \cdot \ln k\,(\mathbf{1}+\mathbf{4}) \\
&\quad - (2.2136 \pm 0.5648);\ R^2 = 0.7081,\ N = 9
\end{aligned} \tag{17}
$$

$$
\ln k\,(\mathbf{1}+\mathbf{14}) = (0.99 \pm 0.03) \cdot \ln k\,(\mathbf{1}+\mathbf{4}) + (0.67 \pm 0.06);\quad R^2 = 0.9912,\ N = 9 \tag{18}
$$

For the ene reactions (**1**+**2**), (**1**+**4**), and (**1**+**14**), as well as the Diels-Alder reaction (**1**+**17**), a high proportionality of the solvent effect on the reaction rate with the angular coefficient close to one has been observed. The close solvent effect on the rate of different reactions presupposes a slight difference in the solvent effect on the energy level of the transition state.

4 | CONCLUSIONS

Ene reactions of structurally similar bicyclic **2** and **4** monoterpenes with **1** go with nearly the same energy and volume parameters: enthalpy, entropy, Gibbs free energy of activation, reaction enthalpy, activation volume, and reaction volume. A high proportionality in the solvent effect on the reaction rate of the reactions **1+2** → **3** and **1+4** → **5** is observed. In a series of nine solvents, the rate of these reactions changes by two orders of magnitude but not due to the solvent polarity, which is similar to other reactions of ene synthesis as well as cycloaddition reactions. The ratio of activation volume to reaction volume ($\Delta V^{\neq}_{\mathrm{corr}}/\Delta V_{r\text{-}n}$) for the reaction **1+2** → **3** is 1.25, and for the **1+4** → **5** $\Delta V^{\neq}_{\mathrm{corr}}/\Delta V_{r\text{-}n}$ is 1.18. Low solvent polarity effect on the reaction rates suggests that there is no solvent electrostriction. Such ratio of volume parameters can be explained by the cyclic and, therefore, more compact form of the transition state in comparison with the acyclic form of the reaction adduct.

DECLARATION OF INTEREST STATEMENT

The authors hereby confirm they have no conflicts of interest.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (Projects No. 16-03-00071 and 18-33-00063), the Ministry of Education and Science of Russian Federation (Project No 4.6223.2017/9.10), and the research grant of Kazan Federal University.

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How to cite this article: Kiselev VD, Kornilov DA, Anikin OV, Shulyatiev AA, Kolesnikova AO, Konovalov AI. Kinetics of the ene reactions of 4-phenyl-1,2,4-triazoline-3,5-dione with β-pinene and 2-carene: temperature, high pressure, and solvent effects. *Int J Chem Kinet*. 2018;50:651–658. https://doi.org/10.1002/kin.21189