Research Article

Journal of Physical Organic Chemistry

Received: 30 October 2013, Revised: 12 December 2013, Accepted: 15 December 2013,

(wileyonlinelibrary.com) DOI: 10.1002/poc.3277

4-Phenyl-1,2,4-triazoline-3,5-dione in the ene reactions with cyclohexene, 1-hexene and 2,3-dimethyl-2-butene. The heat of reaction and the influence of temperature and pressure on the reaction rate

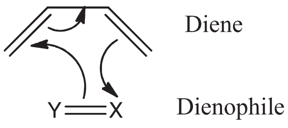
Vladimir D. Kiselev[a]*, Dmitry A. Kornilov[a], Helen A. Kashaeva[a], Lyubov N. Potapova[a] and Alexander I. Konovalov[a]

The values of the enthalpy (53.3; 51.3; 20.0 kJ mol^{-1}), entropy (−106; −122; −144 J mol^{-1}K^{-1}), and volume of activation (−29.1; −31.0; −cm^3 mol^{-1}), the reaction volume (−25.0; −26.6; −cm^3 mol^{-1}) and reaction enthalpy (−155.9; −158.2; −150.2 kJ mol^{-1}) have been obtained for the first time for the ene reactions of 4-phenyl-1,2, 4-triazoline-3,5-dione 1, with cyclohexene 4, 1-hexene 6, and with 2,3-dimethyl-2-butene 8, respectively. The ratio of the values of the activation volume to the reaction volume ($\Delta V^{\neq}_{corr}/\Delta V_{r-n}$) in the ene reactions under study, 1 + 4→5 and 1 + 6→7, appeared to be the same, namely 1.16. The large negative values of the entropy and the volume of activation of studied reactions 1 + 4→ 5 and 1 + 6→7 better correspond to the cyclic structure of the activated complex at the stage determining the reaction rate. The equilibrium constants of these ene reactions can be estimated as exceeding 10^{18} L mol^{-1}, and these reactions can be considered irreversible.

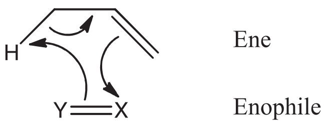
Keywords: activation volume; cyclohexene; 2,3-dimethylbytene-2; ene-reaction; enthalpy reaction; 1-hexene; high pressure effect; 4-phenyl-1,2,4-triazolin-3,5-dione; rate constant

INTRODUCTION

There are some papers dealing with the study of behavior of 4-substituted 1,2,4-triazoline-3,5-dione (TAD) in thermal and photochemical [4 + 2]-, [3 + 2]-, [2 + 2]-cycloaddition, ene and curing reactions.[1–11] An extensive study of the products structure, the reaction rate and the solvent effect on the reaction of [4 + 2]-cycloaddition of **1** with various 1,3-dienes was presented.[1–5] Practically, at the same time, the ene synthesis of **1** with various alkenes was initiated.[5–11] *N*-allylurazole derivatives, the ene reaction products, are usually formed when the allyl hydrogen atom is present in alkene as well as α-shift of the double bond in the product is possible.[9–11]



Diels-Alder Reaction



Ene reaction

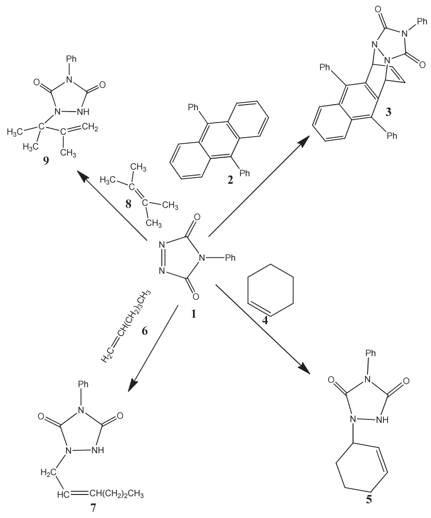
The high activity of the substituted TAD is rationalized by the enhanced easiness of breaking endocyclic π-N = N bond.[12] The acceptor properties and exothermicity of the Diels–Alder reactions (DAR) between 4-phenyl-1,2,4-triazoline-3,5-dione **1** and the C = C analogue, 4-phenylmaleimide, are comparable, whereas the rate of reaction with **1** is 5–6 orders of magnitude higher than that of the C = C analogue.[12] The relatively high thermal stability of the [4 + 2]-cycloaddition adducts coupled with the increased reaction rate allowed TAD to participate in many thermal DARs with usual dienes, as well as with very inactive dienes such as hexachlorocyclopentadiene,[2,3] norbornadiene[2,12] and even with naphthalene and methyl-substituted naphthalene.[13] 9,10-Diphenylanthracene **2** does not normally react with all known dienophiles possessing the C = C bond due to the complete steric shielding of the 9,10-diene reaction centers. Unexpectedly, the reaction **1 + 2→3** takes place even at room temperature at 1,4-atoms of diene **2**, which are less active, but sterically accessible (s 1).[14]

For the ene reactions of TAD with alkenes, the presence of intermediates such as an aziridinium imide, 1,2-, 1,4-dipolar intermediates[9,11,15,16] and biradical has been proposed.[17] However, the effect of the solvent polarity on the rate of the ene reactions with **1** in most cases is very small, and an increased rate is usually observed in the low-polar media.[8] According to the correlation of

---

* *Correspondence to: V. D. Kiselev, Department of Physical Chemistry, Butlerov Institute of Chemistry, Kazan Federal University, Kremlevskaya str. 18, Kazan, 420008, Russian Federation.*
E-mail:vkiselev.ksu@gmail.com

a *V. D. Kiselev, D. A. Kornilov, H. A. Kashaeva, L. N. Potapova, A. I. Konovalov*
Department of Physical Chemistry, Butlerov Institute of Chemistry, Kazan Federal University, Kremlevskaya str. 18, Kazan, 420008, Russian Federation



Scheme 1. 4-Phenyl-1,2,4-triazoline-3,5-dione **1** in the Diels–Alder reaction at 1.4-atoms of 9.10-diphenylanthracene **2**, and in the ene reactions with cyclohexene **4**, 1-hexene **6** and 2,3-dimethyl-2-butene **8**

the solvent effect on the rate of the ene reactions with **1** (ln$k_{(1)}$)[8,9,11] and the DARs with **1** (ln$k_{(2)}$)[12], the following equation was obtained: ln$k_{(1)} = (0.9 \pm 0.1)\ln k_{(2)}$ +1.5; R = 0.974, N = 6. Very similar solvent effect on the rate constants of these reactions generates the slope close to unity.

In comparison with the DARs, the ene reactions with the C = C bond in enophile usually possess higher activation energy (about 100–150 kJ mol^{-1}), while the activation entropies are near the same (about −120 – −170 J mol^{-1}K^{-1}).[18] The concerted mechanism for the retro-ene reaction was proposed on the base of Arrhenius parameter as the firmly established one.[19,20] The same mechanism should be considered for the direct ene-reaction.

Due to their low activity, only few ene reactions with the C = C and C = O reaction centers in the enophiles have been studied under the high pressure and at elevated temperatures.[21–25] The necessity to recalculate the values of the activation volume within the range of temperatures from the high to room one causes the additional errors.[21–25]

It is interesting to compare the activation parameters of the ene reactions and the Diels–Alder ones with **1**. It should be noted that the pressure effect on the rate of alkenes ene reactions with TAD has not been studied. 4-Phenyl-1,2,4-triazoline-3,5-dione **1** is very convenient for such measurements in the reactions **1 + 4→5** and **1 + 6→7** at 25 °C. Taking into account everything above, we studied the effect of temperature and pressure on the rate of ene reactions and compared the values of enthalpy, entropy and volume of activation, enthalpy and volume of reactions **1 + 4→5**, **1 + 6→7** and **1 + 8→9** with those for the DAR. Due to a very fast reaction rate, the pressure effect on the reaction **1 + 8→9** was not studied.

EXPERIMENTAL

Materials

Cyclohexene **4**, 1-hexene **6** (Acros, 99 + %) and 2,3-dimethyl-2-butene **8** (Sigma-Aldrich >98%) were used as purchased. 4-Phenyl-1,2, 4-triazoline-3,5-dione **1** (Aldrich, Germany, 97%) was sublimed at 100 °C and 100 Pa before the measurements. The spectral purity of **1** was analyzed in accordance with the known absorption coefficients ($\varepsilon_{532\ \mathrm{nm}} = 171$ in 1,4-dioxane at 25 °C,[3] $\varepsilon_{540\ \mathrm{nm}} = 245$ in toluene) and by means of spectrophotometric titration of **1** in the fast reaction with scintillating anthracene. The structures of the reaction products **5, 7** and **9** were proved earlier.[7] All solvents were purified by known methods.[26]

Kinetic measurements

The rate of reactions **1 + 4→5** and **1 + 6→7** was determined by measuring the UV absorption of enophile **1** at 530–540 nm (the UV-spectrophotometer Hitachi-2900), where other compounds are transparent. The initial concentration of **1** was in the range of (3–5) · 10^{-3} mol L^{-1} and that of **4** and **6** – (1–2) · 10^{-1} mol L^{-1}. Temperature accuracy was ±0.1 °C. The rate of fast reaction **1 + 8→9** was measured by the stopped-flow method (RX 2000 with spectrophotometer Cary 50 Bio) in benzene solution at 23.3 °C and 40.1 °C and in 1,2-dichloroethane solution at 23.5 °C by monitoring the absorption of **1** at 540 nm. The concentration of **1** stock solutions was 8.13·10^{-3} mol L^{-1} and that of **8** was 8.86·10^{-2} mol L^{-1}. The values of the rate constants were determined with errors of ±3%, the enthalpy of activation – ±2 kJ mol^{-1} and the entropy of activation – ±6 J mol^{-1} K^{-1}.

The rate constants of reactions **1 + 4→5** and **1 + 6→7** under elevated pressure were measured in toluene solution at 25 °C with the high pressure system, using the high pressure-pump "HP-500" and the high pressure optical cell "PCI-500" produced by Syn. Co., Ltd (Japan), adjusted to our UV-spectrophotometer (SCINCO Co., Ltd, Seoul, Korea).

Calorimetry

The enthalpies of all the studied reactions in solution were measured at 25 °C by calorimetric method, described previously.[12] The solid sample (20–35 mg) of **1** was added to the solution of cyclohexene **4** in toluene (150 mL, $c_4 = 1.0$ mol L^{-1}). Four consecutive measurements for reaction **1 + 4→5** provided: −138.0, −137.8, −136.8 and −137.8 kJ mol^{-1}. With the heat of solution of solid **1** in toluene (18.3 kJ mol^{-1}), the enthalpy of reaction **1 + 4→5** in toluene solution is −155.9 ±0.4 kJ mol^{-1}. Three consecutive measurements of the heat of reaction **1 + 6→7** in 1,2-dichloroethane solution provided: −136.1, −135.1 and −137.8 kJ mol^{-1}. With the heat of solution of solid **1** in 1,2-dichloroethane (21.9 kJ mol^{-1}), the enthalpy of reaction **1 + 6→7** in 1,2-dichloroethane solution is −158.2 ±1.0 kJ mol^{-1}. The heat of reaction **1 + 8→9** was measured in toluene (−121.9; −120.3 and −120.6 kJ mol^{-1}) as well as in 1,2-dichloroethane (−127.1; −130.2 and −127.4 kJ mol^{-1}). Taking into account the heat of solution of solid **1**, the enthalpy of reaction **1 + 8→9** is −139.2 ± 0.6 kJ mol^{-1} in toluene and −150.2 ± 1.4 kJ mol^{-1} in 1,2-dichloroethane, respectively.

Volume parameters

The volume of activation, $\Delta V^{\neq}$, was calculated using the dependence lnk_p *vs P*, where k_p is the rate constant of reactions **1 + 4→5** and **1 + 6→7** carried out under pressure *P*. Reactions **1 + 8→9** were very fast for such measurements.

The reaction volume (ΔV_{r-n}) was calculated using Eqn (1)[12]:

$$1/d_{(t)} = 1/d_{(t=0)} + c_{\mathbf{Add},t}\,\Delta V_{r-n}/1000d_{(t=0)} \qquad (1)$$

Here, $c_{\mathbf{Add},t}$ is the current concentration of **5** or **7** adduct, $d_{(t=0)}$ and d_t are the initial and current densities of solution of the reaction mixture, ΔV_{r-n} is the reaction volume. The vibration densimeter manufactured by Anton Paar, model DSA 5000M, was employed for the measurements of the solution density at 25 ± 0.002 °C. The densimeter was calibrated with water and air, in accordance with the manual.

RESULTS AND DISCUSSIONS

Kinetic measurements at ambient pressure

The rate constants of reactions **1 + 4→5, 1 + 6→5** and **1 + 8→9** in temperature range as well as the activation parameters are summarized in Table 1.

It can be noted that the rate constants and activation parameters for the ene-reactions of **1 + 4→5** and **1 + 6→7** are nearly the same. The reaction rate of **1** with tetramethylethylene **8** is higher on four orders of magnitude, mainly due to a very low enthalpy of activation. All the kinetic data obtained for the ene synthesis with **1** are more consistent with the asymmetric formation of new C–N and N–H bonds, which does not preclude their concerted formation.[5] The large and negative values of the activation entropy in the studied ene reactions (Table 1) are similar to those of the Diels–Alder reaction[12,27] and correspond to a highly ordered transition state.

It is interesting to find out what determines the change of alkenes activity in the ene reactions with **1**. The values of alkenes ionization potentials of (*IP*/eV),[28] and their reaction rate constants (lnk_2) with **1** in dichloromethane,[9] are collected in Table 2.

As it can be seen from Fig. 1, the definite increase of the ene reactions rate with that of π-donor properties of alkenes has been observed. Similar linear relations lnk_2 *vs IP* of the dienes are typical for the DARs.[27]

The enthalpies of the studied ene reactions (from −139 to −158 kJ mol^{-1}) are more exothermic than those of the Diels–Alder reactions of **1** with substituted anthracenes (from −50 kJ mol^{-1} to −118 kJ mol^{-1}), and **1** with cyclopentadiene (−134 kJ mol^{-1}), but less exothermic than in reaction of **1** with 1,3-butadiene (−201 kJ mol^{-1}) and norbornadiene (−218 kJ mol^{-1}).[12]

Table 2. The adiabatic ionization potentials of some acyclic alkenes (IP_{ad}/eV) and the rate constants of the ene reactions alkenes with **1** (lnk_2/k_2 in L mol^{-1} s^{-1}) in dichloromethane at 23.5 °C

No	Alkene	IP_{ad}	lnk_2
1.	2,3-Dimethylbutene-2	8.27	5.81[a]
2.	2-Methylbutene-2	8.68	1.87
3.	*cis*-Hexene-3	8.95	−0.115
4.	*cis*-Butene-2	9.11	−0.967
5.	*trans*-Butene-2	9.10	−1.71
6.	2-Methylpropene	9.24	−1.64
7.	Hexene-1	9.46	−4.61

[a] Data of this work in 1,2-dichloroethane at 23.5 °C.

Kinetic measurements under high pressure

The experimental values of the activation volume were calculated from Eqn (2). The rate constants of the under pressure reactions were obtained by admitting the initial concentrations of reagents as independent of the pressure.

$$\Delta V^{\neq}{}_{\mathrm{app}} = -RT\,\partial \ln(k_{\mathrm{P}})/\partial P \tag{2}$$

The corrected value ($\Delta V^{\neq}_{\mathrm{corr}}$) of the activation volume can be calculated taking into account the compression of the solvent[29]:

$$\Delta V^{\neq}{}_{\mathrm{corr}} = -RT\,\partial \ln(k_{\mathrm{P}})/\partial P + (n-1)RT\beta_{\mathrm{T}} \tag{3}$$

Here, k_{P} is the rate constant of the reaction under pressure calculated without the correction of the concentration value (*m*, *c*, *x*)

Table 1. The rate constants (k_2/L mol^{-1} s^{-1}), enthalpy ($\Delta H^{\neq}$/kJ mol^{-1}), entropy ($\Delta S^{\neq}$/J mol^{-1} K^{-1}) and free energy ($\Delta G^{\neq}$/kJ mol^{-1}) of activation for the ene reactions **1 + 4 → 5; 1 + 6 → 7** and **1 + 8 → 9**

T/°C	k_2	*R* [a]	*N* [b]	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
Reaction **1 + 4 → 5** in toluene						
15.0	$3.84\cdot10^{-3}$	0.9999	76	53.3	−106	84.9
20.0	$5.51\cdot10^{-3}$	0.9999	54			
25.0	$8.07\cdot10^{-3}$	0.9999	51			
25.0	$7.91\cdot10^{-3}$	0.9999	24			
26.0	$8.58\cdot10^{-3}$	0.9999	95			
40.0	$24.3\cdot10^{-3}$	0.9997	60			
Reaction **1 + 6 → 7** in toluene						
15.0	$1.15\cdot10^{-3}$	0.9999	19	51.8	−122	88.1
25.0	$2.33\cdot10^{-3}$	0.9998	15			
25.0	$2.35\cdot10^{-3}$	0.9999	22			
25.0	$2.32\cdot10^{-3}$	0.9997	21			
25.0	$2.37\cdot10^{-3}$	0.9999	17			
40.0	$6.90\cdot10^{-3}$	0.9998	15			
Reaction **1 + 8 → 9**						
23.3	55.6 ± 0.5 [c]	≥0.9998 [c]	≥63 [c]	20.0	−144	62.9
40.1	90.5 ± 1.3 [c]	0.9999 [c]	≥43 [c]			
23.5	335 ± 9 [d]	≥0.9998 [d]	≥15 [d]			

[a] *R* is the correlation coefficient.

[b] *N* is the number of points in reaction run.

[c] The mean values of ten repeated measurements of reaction rate in benzene;

[d] The mean values of ten repeated measurements in 1,2-dichloroethane.

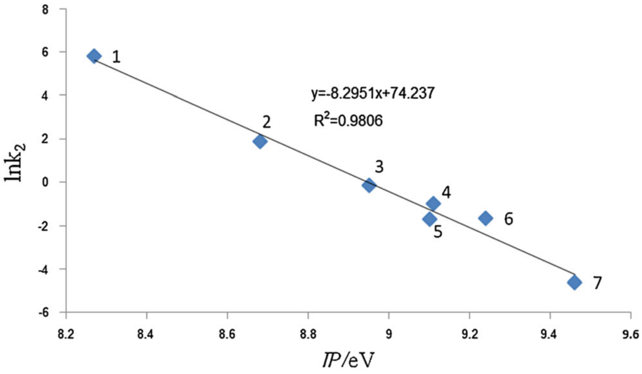


Figure 1. The dependence of the rate constant (lnk_2) of the ene reactions 4-phenyl-1,2,4-triazoline-2,5-dione with alkenes on their ionization potentials (*IP*/eV). The numbering of the points corresponds to Table 2

under pressure *P*, and $(n-1)RT\beta_T$ is the correction item, where *n* is the reaction order, and $\beta_T = \partial \ln(d)/\partial P$ is the solvent compressibility coefficient. The experimental values of the rate constants under pressure are summarized in Table 3.

The rate of reaction **1** + **4** → **5** was followed by the change of the absorption of enophile **1** at the comparable stock concentrations of the reagents: $c_{0,\mathbf{1}} = 0.0103$ and $c_{0,\mathbf{4}} = 0.0202$ mol L^{-1}, (Fig. 2). The stock concentrations of reagents $c_{0,\mathbf{1}} = 0.0061$ and $c_{0,\mathbf{6}} = 0.0622$ mol L^{-1} were used for the slower rate of reaction **1** + **6** → **7** (Fig. 3). All the reaction mixtures were prepared from the stock solutions of reagents to decrease the errors in ratio Ln($k_P/k_{P=1}$).

The rate constants of reaction **1** + **4** → **5** under pressure were calculated on the basis of the absorption coefficient ε_1 in toluene (245 L mol^{-1} cm^{-1}, $\lambda_{max} = 540$ nm) and its alterations under pressure: $\varepsilon_{\mathbf{1},P}$ (540 nm) = 245 + 0.0428*P* – 3.83 10^{-6} P^2, R = 0.9998, N = 5. The dependence of the reaction rate on the pressure (line *a*, Fig. 4) was described by polynomial Eqn (4) as well as logarithmically (5).

$$\mathrm{Ln}(k_P/k_{P=1}) = -0,0299 + 1.269{\cdot}10^{-3}P - 1.62{\cdot}10^{-7}P^2; \quad R^2 = 0,9990; \mathrm{N} = 10 \qquad (4)$$

$$\mathrm{Ln}(k_P/k_{P=1}) = 3.535\mathrm{Ln}[(2844 + P)/2844]; R^2 = 0,9976; \quad \mathrm{N} = 10 \qquad (5)$$

Table 3. Pressure (*P*/bar) effect on the rate constant (k_2/L mol^{-1} s^{-1}) of the reactions **1** + **4**→**5** and **1** + **6**→**7** in toluene at 25 °C

Reaction **1** + **4** → **5**			Reaction **1** + **6** → **7**		
P	k_2	Ln($k_P/k_{P=1}$)	*P*	k_2	Ln($k_P/k_{P=1}$)
1	0.00778	0	1	0.00204	0
219	0.00972	0.223	214	0.00285	0.336
336	0.0110	0.349	431	0.00369	0.592
594	0.0152	0.667	628	0.00447	0.784
783	0.0188	0.883	816	0.00544	0.980
1034	0.0233	1.097	1025	0.00671	1.190
1296	0.0297	1.341	1313	0.0084	1.415
1578	0.0385	1.599	1618	0.0105	1.638
1793	0.0438	1.729	2013	0.0136	1.898
1987	0.0488	1.836			

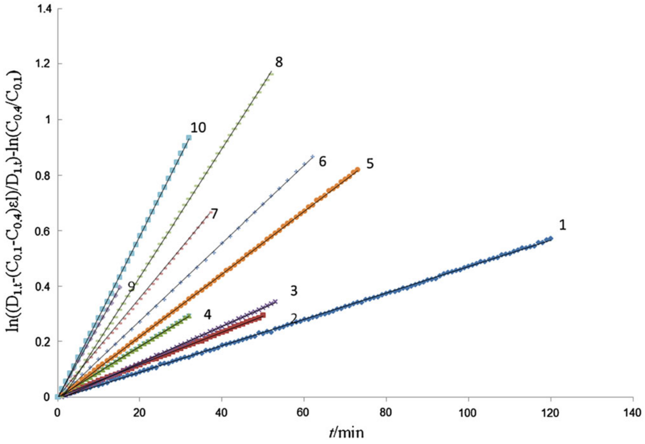


Figure 2. Pressure effect on the rate of reaction **1** + **4**→**5** in toluene at 25 °C: 1 – 1; 2 – 219; 3 – 336; 4 – 594; 5 – 783; 6 – 1034; 7 – 1296; 8 –1578; 9 – 1793 and 10 – 1987 bar

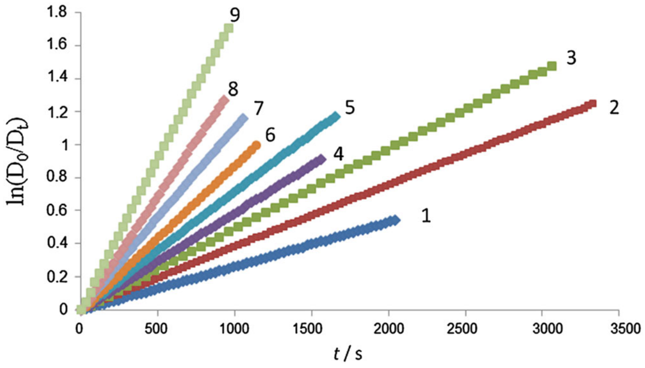


Figure 3. Pressure effect on the rate of reaction **1** + **6**→**7** in toluene at 25 °C: 1 – 1; 2 – 214; 3 – 431; 4 – 628; 5 – 816; 6 – 1025; 7 – 1313; 8 –1618 and 9 – 2013 bar

According to Eqns (4) and (2), the experimental value of activation volume, $\Delta V^{\neq}_{app}$, is equal to −31.3 ± 0.5 cm^3 mol^{-1}. The corrected value of $\Delta V^{\neq}_{corr}$ was calculated according to Eqn (3) with the compressibility coefficient of toluene, $\beta_T = 90{\cdot}10^{-6}$ bar[30] and is equal to −29.1 ± 0.5 cm^3 mol^{-1}. In accordance with the independent logarithmic relation (5), the values of $\Delta V^{\neq}_{app}$ and $\Delta V^{\neq}_{corr}$ are calculated as −30.7 ± 0.9 and −28.5 ±0.9 cm^{3}mol^{-1}, respectively. Relation (4) has the better correlation coefficient than the logarithmic one (5). However, Eqn (4), in contrast to Eqn (5), implies the existence of the false peak at *P* = 3920 bar, and the reaction rate [Ln($k_P/k_{P=1}$)] under higher pressure cannot be predicted. It should be noted that the difference in two values of $\Delta V^{\neq}$ at *P* = 1 is within experimental error. Equation (5) is applicable for the determination of the activation volume and is also useful when choosing the conditions of the reaction under pressure. For instance, Eqn (5) predicts value $k_P/k_{P=1}$ equal to 206 at 10 kbar and 660 at 15 kbar, respectively.

The rate of slower reaction **1** + **6**→**7** under pressure was studied with account of the pseudo first-order conditions (Fig. 3). The pressure effect on the reaction rate (Fig. 4, line *b*) was described by polynomial Eqn (6).

$$\mathrm{Ln}(k_P/k_{P=1}) = \ 0,030 + 1.338{\cdot}10^{-3}P - 2.08{\cdot}10^{-7}P^2; \quad R^2 = 0,9990; \mathrm{N} = 9 \qquad (6)$$

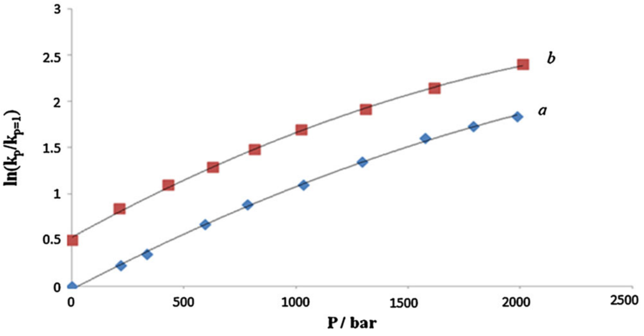


Figure 4. Correlation $\ln(k_p/k_{p=1})$ *vs P* for ene reaction $\mathbf{1+4 \to 5}$ (*a*) and for reaction $\mathbf{1+6 \to 7}$ (*b*) in toluene at 25 °C. For clarity, the line *b* shifted up on the value of 0.5

The values of $\Delta V^{\neq}_{app}$ (-33.2 cm^{3}mol^{-1}) and $\Delta V^{\neq}_{corr}$ (-31.0 cm^{3}mol^{-1}) for the ene reaction $\mathbf{1+6 \to 7}$ were obtained from these data.

It is important to compare the volume of activation and that of reaction. In this work, we used a more convenient method, namely, Eqn (1), to determine the reaction volume. Linear dependences $1/d_{(t)}$ *vs* $c_{\mathbf{5},t}$ or $c_{\mathbf{7},t}$ have been obtained for up to 100% of conversion for reactions $\mathbf{1+4 \to 5}$ (Fig. 5) and $\mathbf{1+6 \to 7}$ (Fig. 6).

The mean value of the $\mathbf{1+4 \to 5}$ reaction volume, ΔV_{r-n}, is -25.0 ± 0.4 cm^3 mol^{-1}, and the ratio $\Delta V^{\neq}_{corr}/\Delta V_{r-n}$ is $-29.1/-25.0$ equal to 1.16. For the ene reaction $\mathbf{1+6 \to 7}$, the same ratio was obtained: $-31.0/-26.6 = 1.16$. This suggests that the volume of the activated complex of reactions $\mathbf{1+4 \to 5}$ and $\mathbf{1+6 \to 7}$ in toluene is smaller by 16% than that of the products **5** and **7**. The data available,[8,9,11] showing the weak influence of the solvent polarity on the reaction rate, allow to exclude the solvent electrostriction in the solvation shell of the activated complex as the main cause resulting in this ratio: $\Delta V^{\neq}_{corr}/\Delta V_{r-n}$ 1. This "abnormal" ratio ($\Delta V^{\neq}_{corr}/\Delta V_{r-n} > 1$) in the isopolar DARs was explained by different possibilities of the solvent molecules to fit the large steric hindered structures of the cyclic activated complex and cyclic adducts.[31] A more suitable explanation of the results obtained ($\Delta V^{\neq}_{corr}/\Delta V_{r-n} > 1$) for studied ene reactions $\mathbf{1+4 \to 5}$ and $\mathbf{1+6 \to 7}$ can result from the assumption of the formation of more compact cyclic structure of the activated complex when compared to the noncyclical structure of reaction products **5** and 7. This conclusion is in agreement with the results of earlier investigations in the field of the ene reactions of alkenes and enophiles with the C=O and C≡C reaction centers,[24,25,32] where ratio $\Delta V^{\neq}/\Delta V_{r-n}$, recalculated for 25 °C, was in the range of 1.1–1.3. The ratio for the ene reaction with diethyl azodicarboxylate needs to be tested.[32] Van der Waals molar volumes were calculated for the model ene reaction of propylene (35.1 cm^{3}mol^{-1}) and ethylene (25.6 cm^{3}mol^{-1}) with the formation of the activated complex in this ene reaction (54.6 cm^{3}mol^{-1}) and the product, 1-pentene, (55.8 cm^{3}mol^{-1}).[33,34] The activated complex should be more compact than the product of this ene reaction, which follows from these data of *ab initial* calculations ($\Delta V^{\neq}_W/\Delta V_{r-n,W} = 1.15$).[33,34]

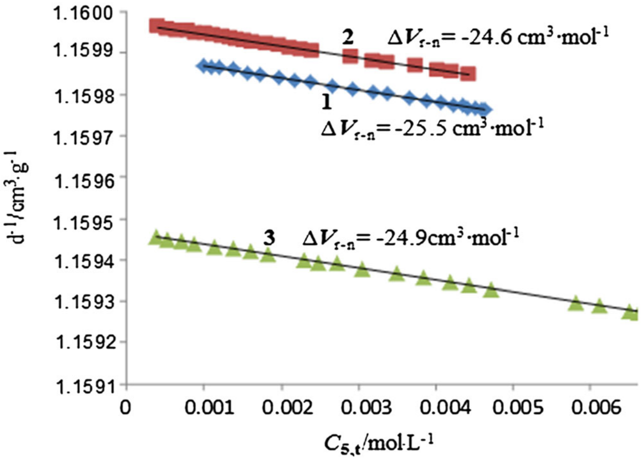


Figure 5. Relation d^{-1} (cm^3 g^{-1}) *vs* $C_{\mathbf{5},t}$ (mol L^{-1}) for reaction $\mathbf{1+4 \to 5}$ in toluene at 25 ± 0.002 °C. **1**. $d^{-1} = -0.0296\ C_{\mathbf{5},t}\ +1.1599$; $R^2 = 0.9996$; $C_{01} = 4.577 \cdot 10^{-3}$ mol·L^{-1}; $C_{04} = 5.732 \cdot 10^{-2}$ mol·L^{-1} **2**. $d^{-1} = -0.0285\ C_{\mathbf{5},t}\ +1.1600$; $R^2 = 0.9992$; $C_{01} = 4.482 \cdot 10^{-3}$ mol·L^{-1}; $C_{04} = 6.603 \cdot 10^{-2}$ mol·L^{-1} **3**. $d^{-1} = -0.0289\ C_{\mathbf{5},t}\ +1.1595$; $R^2 = 0.9996$; $C_{01} = 6.806 \cdot 10^{-3}$ mol·L^{-1}; $C_{04} = 3.092 \cdot 10^{-2}$ mol·L^{-1}

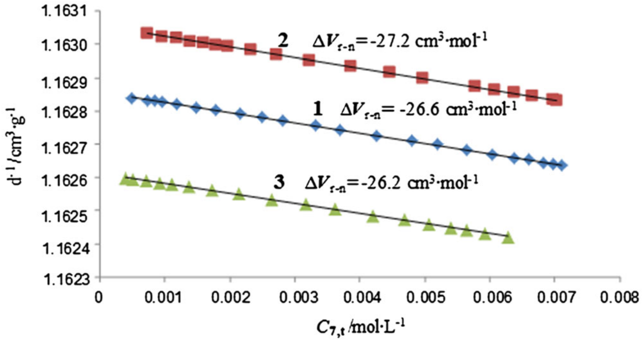


Figure 6. Relation d^{-1} (cm^3 g^{-1}) *vs* $c_{\mathbf{7},t}$ (mol L^{-1}) for reaction $\mathbf{1+6 \to 7}$ in toluene at 25 ± 0.002 °C. **1**. $d^{-1} = -0.030935 C_{\mathbf{7}}\ +1.162857$; $R^2 = 0.9997$; $C_{01} = 6.986 \cdot 10^{-3}$ mol L^{-1}; $C_{0\mathbf{6}} = 0.12495$ mol L^{-1}. For clarity, the line **1** shifted down on the value of 0.0002; **2**. $d^{-1} = -0.031638\ C_{\mathbf{7}}\ +1.163056$; $R^2 = 0.9997$; $C_{01} = 7.172 \cdot 10^{-3}$ mol L^{-1}; $C_{0\mathbf{6}} = 0.1246$ mol L^{-1}; **3**. $d^{-1} = -0.030409\ C_{\mathbf{7}}\ +1.162612$; $R^2 = 0.9994$; $C_{01} = 6.90 \cdot 10^{-3}$ mol L^{-1}; $C_{0\mathbf{6}} = 0.1114$ mol L^{-1}

CONCLUSIONS

To sum up everything above, we can say that we obtained the values of the enthalpy, entropy and volume of activation, the reaction volume and the enthalpy of ene-reactions of 4-phenyl-1,2,4-triazoline-3,5-dione with cyclohexene, 1-hexene and 2,3-dimethyl-2-butene. It can be assumed that the large negative values of the entropy ($\Delta S^{\neq} = -106$ and -122 J mol^{-1} K^{-1}) and volume of activation ($\Delta V^{\neq}_{corr} = -26.6$ and -29.1cm^3 mol^{-1}) of the $\mathbf{1+4 \to 5}$ and $\mathbf{1+6 \to 7}$studied reactions are in good agreement with the assumption that the activated complex on the stage determining the ene reaction rate has the cyclic structure. Very small solvent polarity effect on the ene reaction rate,[8,9,11] similar to the solvent effect in the DARs,[3,12,27] excludes the charge generation in the transition state. In both reactions under study, namely, $\mathbf{1+4 \to 5}$ and $\mathbf{1+6 \to 7}$, the value $\Delta V^{\neq}/\Delta V_{r-n}$ is 1.16, which is in agreement with the previous assumptions[24,25,32–34] that there is a more compact volume of cyclic activated complex when compared with the noncyclical ene products.

It was observed (Fig. 1) that the reaction rate of acyclic alkenes with 4-phenyl-1,2,4-triazoline-3,5-dione is proportional to the π-donor properties of alkenes.

Polynomial (4) and logarithmic (5) equations both give the same value of the activation volume at $P = 1$ bar. However, only

Eqn (5) can predict the pressure effect on the reaction rate under high pressure.

The values of the heat of ene reactions with **1** are reported for the first time. High exothermicity of the studied reactions (−155.9 for **1** + **4** → **5** in toluene; −158.2 for **1** + **6** → **7** in 1, 2-dichloroethane; −139.2 for **1** + **8** → **9** in toluene, and −150.2 in 1,2-dichloroethane) allows us to consider these ene reactions as irreversible under standard conditions. The equilibrium constants of the ene-reactions studied can be estimated as exceeding 10^{18} L mol^{-1}.

Acknowledgements

The authors thank the Joint Project of the USA Civilian Research and Development Foundation and High Education of the Russian Federation (Project BRHE REC-007), and the Russian Foundation for the Basic Research (Project No 12-03-00029) for the financial support. We also highly appreciate the fruitful comments of the reviewers, which helped us to finalize this manuscript.

REFERENCES

[1] R. C. Cookson, S. S. H. Gilani, I. D. R. Stevens, *J. Chem. Soc., C.* **1967**, 1905.
[2] M. E. Burrage, R. C. Cookson, S. S. Gupte, I. D. R. Stevens, *J. Chem. Soc., Perkin Trans. II* **1975**, 1325 (and Refs therein).
[3] J. Sauer, B. Schröder, *Chem. Ber.* **1967**, *100*, 678.
[4] A. I. Konovalov, I. P. Breus, I. A. Sharagin, V. D. Kiselev, *Russian J. Org. Chem.* **1979**, *15*, 361.
[5] I. K. Korobitsina, A. V. Khalikova, L. L. Rodina, N. P. Shusherina, *Chem. Heterocyclic Comp.* **1983**, *19*, 117.
[6] W. H. Pirkle, J. C. Stickler, *Chem. Comm.* **1967**, 760.
[7] S. Ohashi, K. Leong, K. Matyjaszewski, G. B. Butler, *J. Org. Chem.* **1980**, *45*, 3467.
[8] S. Ohashi, G. B. Butler, *J. Org. Chem.* **1980**, *45*, 3472.
[9] C. C. Cheng, C. A. Seymour, M. A. Petti, F. D. Green, *J. Org. Chem.* **1984**, *49*, 2910.
[10] H. M. R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 556.
[11] W. Adam, N. Carballeira, *J. Am. Chem. Soc.* **1984**, *106*, 2874.
[12] V. D. Kiselev, I. I. Shakirova, D. A. Kornilov, H. A. Kashaeva, L. N. Potapova, A. I. Konovalov, *J. Phys. Org. Chem.* **2013**, *26*, 47.
[13] G. W. Breton, K. A. Newton, *J. Org. Chem.* **2000**, *65*, 2863.
[14] V. D. Kiselev, I. I. Shakirova, H. A. Kashaeva, L. N. Potapova, D. A. Kornilov, D. B. Krivolapov, A. I. Konovalov, *Mendeleev Comm.* **2013**, *23*, 235.
[15] S. F. Nelsen, D. L. Kapp, *J. Am. Chem. Soc.* **1985**, *107*, 5548.
[16] M. Fujita, H. Matsushima, T. Sugimura, A. Tai, T. Okuyama, *J. Am. Chem. Soc.* **2001**, *123*, 2946.
[17] D. A. Singleton, C. Hang, *J. Am. Chem. Soc.* **1999**, *121*, 11885.
[18] B. Franzus, *J. Org. Chem.* **1963**, *28*, 2954.
[19] H. E. O'Neal, S. W. Benson, *J. Phys. Chem.* **1967**, *71*, 2903.
[20] O. Achmatowicz, J. Szymoniak, *J. Org. Chem.* **1980**, *45*, 1228.
[21] G. Jenner, M. Papadopoulos, *J. Org. Chem.* **1982**, *47*, 4201.
[22] R. Ben Salem, G. Jenner, *Tetrahedron Lett.* **1986**, *27*, 1575.
[23] G. Jenner, R. Ben Salem, *Nouv. J. Chem.* **1987**, *11*, 677.
[24] G. Jenner, R. Ben Salem, B. S. El'yanov, E. M. Gonikberg, *J. Chem. Soc., Perkin Trans.2* **1989**, 1671.
[25] B. El'yanov, E. M. Gonigberg, G. Jenner, *J. Chem. Soc., Perkin Trans. 2* **1992**, 137.
[26] J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvents*, 4th edn, John Wiley, New York- Chichester- Brisbane- Toronto- Singapore, **1986**.
[27] V. D. Kiselev, A. I. Konovalov, *J. Phys. Org. Chem.* **2009**, *22*, 466.
[28] M. Montali, A. Credi, L. Prodi, M. T. Gandolf, *Handbook of photochemistry*, 3rd edn, Tailor and Francis Group, LLC, New York, **2006**, Chapter 7.
[29] V. D. Kiselev, *Int. J. Chem. Kin.* **2013**, *45*, 613.
[30] V. D. Kiselev, A. V. Bolotov, A. P. Satonin, I. I. Shakirova, E. A. Kashaeva, A. I. Konovalov, *J. Phys. Chem. B* **2008**, *112*, 6674.
[31] V. D. Kiselev, *Int. J. Chem. Kin.* **2010**, *42*, 117.
[32] K. N. Houk, Y. Li, J. D. Evanseck, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 682.
[33] Y. Li, K. N. Houk, *J. Am. Chem. Soc.* **1993**, *115*, 5414.
[34] F. Wurche, F.-G. Klärner, in: *High Pressure Chemistry*, (Eds: R. van Eldik, F.-G. Klärner), Wiley-VCH, Weineim, **2002**, 77.