

Cycloheptatriene in the Reaction of Ene Synthesis with Diethylazodicarboxylate

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Abstract—The rate of an ene reaction between cycloheptatriene and *trans*-diethylazodicarboxylate in 1,2-dichloroethane was studied at various pressures and temperatures. The results obtained were compared with kinetic parameters of some other reactions.

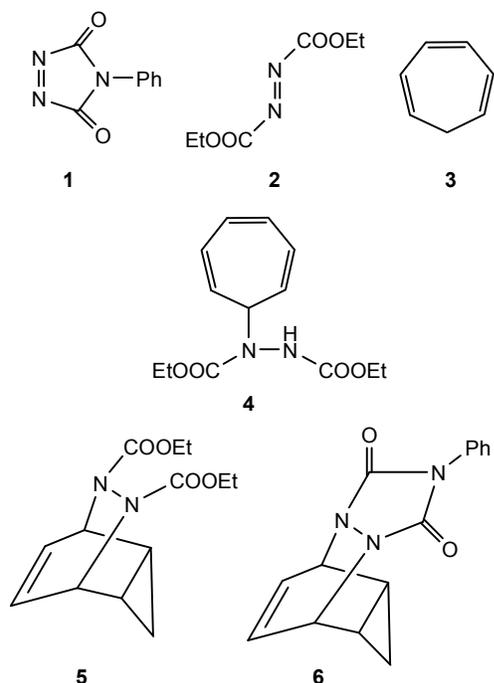
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Reactions of 1,3-diene and ene reagents with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione **1** and *trans*-diethylazodicarboxylate **2** containing N=N reaction sites are of interest due to their wide application in urazoles synthesis and the huge difference in the rate and direction of reactions involving reagents **1** and **2** [1–5]. Heterocyclic diketone **1** in the Diels–Alder reaction is by 5–6 orders of magnitude more active than its C=C structural analog, *N*-phenylmaleimide [6].

Acyclic dienophile **2** contains as well the N=N reaction site, yet its activity in these reactions is nearly by 7 orders of magnitude lower than that of diketone **1** [6]. Diels–Alder reaction involving the latter completed at 25°C in toluene within the time of mixing with cyclopentadiene (k_2 160000), cyclohexadiene (k_2 6100), and cycloheptatriene **3** [k_2 7.57 L mol⁻¹ s⁻¹] [6–8], whereas the analogous process of azodicarboxylate **2** proceeded with a moderate rate even with cyclopentadiene (k_2 3.03 × 10⁻³ L mol⁻¹ s⁻¹) [6]. In the reaction with cyclohexadiene the ene synthesis successfully (4 : 1) competes with the Diels–Alder reaction [9, 10], and with cycloheptatriene under common conditions only the ene synthesis is observed [11]. In the case of steric hindrances for the Diels–Alder reaction azodicarboxylate **2** predominantly reacted along the type of the ene synthesis (**2** + **3** → **4**), whereas diketone **1** easier entered into the reactions of [4+2]-cycloaddition (**1** + **3** → **6**) [6].

In this study we examined the rate of reaction **2** + **3** → **4** at various temperatures and pressures, established the enthalpy, entropy, and activation volume, and also the reaction volume in 1,2-dichloroethane; the obtained parameters were compared with the data for some reactions of ene and diene synthesis involving reagents **1** and **2**.

The following kinetic and activation parameters were obtained for the reaction **2** + **3** → **4** in 1,2-dichloroethane: $k_2 \times 10^4$ 0.612 (25°C), 1.11 (35°C),



2.16 (45°C), 3.83 (55°C) L mol⁻¹ s⁻¹; ΔH^\ddagger 47.4 ± 2 kJ mol⁻¹; ΔS^\ddagger -167 ± 6 J mol⁻¹ K⁻¹, ΔG^\ddagger 97.0 ± 2 kJ mol⁻¹. The activation volume corresponding to the difference between the molar volumes of the activated complex and reagents can be determined only from the dependence of the rate constant $\ln k_2$ on the pressure P . Equation (1) where C and B are constants is more convenient for describing the experimental data than the often applied second order equation since the latter suggests a false maximum at a high pressure [12].

$$\ln(k_P/k_{P=1}) = C \ln[(B + P)/B]. \quad (1)$$

The corrected value of the activation volume ($\Delta V_{\text{corr}}^\ddagger$) at the normal pressure with accounting for the change in the reagents concentration because of the compressibility of the solvent is determined from expression [13]:

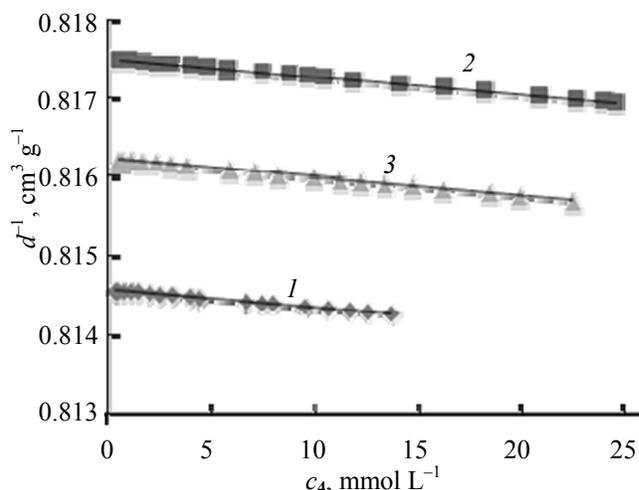
$$\Delta V_{\text{corr}}^\ddagger = -RT \partial \ln(k_P/k_{P=1}) / \partial P + (n - 1)RT\beta_T, \quad (2)$$

where β_T is the compressibility coefficient of 1,2-dichloroethane (80.1×10^{-6} bar⁻¹ at 25°C [14]), n is the kinetic order of the reaction. It was recently demonstrated by the example of nonpolar, polar, and ionic processes, that the ratio of the slopes values $\partial \ln(k_P/k_{P=1}) / \partial P$ at $P = 1$ bar to the slope of the secant at 1000 bar [$\ln(k_{P=1000}/k_{P=1})/1000$] was constant, 1.15 ± 0.03 [15].

$$\partial \ln(k_P/k_{P=1}) / \partial P = (1.15 \pm 0.03) \times 10^{-3} \ln(k_{P=1000}/k_{P=1}). \quad (3)$$

As the determination of $\partial \ln(k_P/k_{P=1}) / \partial P$ at $P = 1$ often occurs with large errors [12], we have calculated this value from eq. (3) using experimental data on reaction $2 + 3 \rightarrow 4$ rate constants obtained in 1,2-dichloroethane at normal pressure (k_2 6.12×10^{-5}) and at 1000 bar [k_2 24.6×10^{-5} L mol⁻¹ s⁻¹] at 25°C. The rate constant of the reaction $2 + 3 \rightarrow 4$ at high pressure was measured using an installation for high pressure equipped with an optic cell PCI-500 (Syn. Co., Japan) adjusted by the size to a spectrophotometer (SCINCO Co, Korea). The measured activation volume of the reaction was $\Delta V_{\text{corr}}^\ddagger$ -38.1 ± 1.1 cm³ mol⁻¹.

In discussing the reaction mechanism it is important to compare the values of the activation volumes ($\Delta V_{\text{corr}}^\ddagger$) and reaction volumes ($\Delta V_{\text{r-n}}$). The difference between these values corresponds to the difference between the volumes of the activated complex and of the reaction product. The value of the reaction volume is conveniently determined from the dependence of the density of the reagents solution in the course of reaction (d_t) on the concentration of the formed adduct ($c_{4,t}$) [16]:



Dependence of the variation in the specific volume of the reaction mixture on the concentration of adduct **4** formed in the reaction of cycloheptatriene **3** with *trans*-diethylazodicarboxylate **2** in 1,2-dichloroethane at $25 \pm 0.002^\circ\text{C}$. **1**: $d^{-1} = -0.022129c_4 + 0.814572$, R^2 0.9995, c_{02} 45.3, c_{03} 0.440 mol L⁻¹, $\Delta V_{\text{r-n}}$ -27.17 cm³ mol⁻¹; **2**: $d^{-1} = -0.022880c_4 + 0.817506$, R^2 0.9999, c_{02} 51.2, mmol L⁻¹, c_{03} 0.548 mol L⁻¹, $\Delta V_{\text{r-n}}$ -27.99 cm³ mol⁻¹; **3**: $d^{-1} = -0.022570c_4 + 0.816225$, R^2 0.9999, c_{02} 050.2 mmol L⁻¹, c_{03} 0.498 mol L⁻¹, $\Delta V_{\text{r-n}}$ -27.65 cm³ mol⁻¹. $\Delta V_{\text{r-n}}$ (av.) -27.60 ± 0.29 cm³ mol⁻¹.

$$1/d_t = 1/d_{t=0} + c_{4,t} \Delta V_{\text{r-n}} / 1000 d_{t=0} \quad (4)$$

We observed in our experiments the corresponding linear dependences (see the figure).

The comparison of kinetic parameters of some Diels–Alder reactions and ene syntheses involving electrophiles **1** and **2** (see the table) shows that the exothermic effect of ene reactions of alkene with diketone **1** is often larger than of the Diels–Alder reaction. It is presumable that Wagner–Meerwein rearrangement in the reaction of compound **1** with norbornene would provide a stable product, since it is accompanied with a large exothermic effect. The kinetically moderate reaction of compound **1** with norbornadiene is accompanied with a maximum exothermic effect corresponding to the absence of the conjugation between the double bonds in this 1,4-diene. It is possible to mark the proportionality between the entropy (ΔS^\ddagger) and the activation volume (ΔV^\ddagger) of the reactions under consideration (r 0.91).

The ratio of the rate constants of the Diels–Alder reaction of cyclopentadiene with acceptors **1** (1.6×10^5) and **2** [3.03×10^{-3} L mol⁻¹ s⁻¹] equals 5.3×10^7 . Taking into account the rate of the analogous reaction of cycloheptatriene with diketone **1** [k_2 7.57 L mol⁻¹ s⁻¹]

Rate constants (k_2), activation enthalpy (ΔH^\ddagger), activation entropy (ΔS^\ddagger), activation volumes (ΔV^\ddagger), enthalpy (ΔH_{r-n}), and volumes (ΔV_{r-n}) of a number of reactions of 4-phenyl-1,2,4-triazoline-3,5-dione **1** and diethylazodicarboxylate **2**, toluene, 25°C

Reaction type	k_2 , L mol ⁻¹ s ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	$-\Delta S^\ddagger$, J mol ⁻¹ K ⁻¹	$-\Delta V^\ddagger/-\Delta V_{r-n}$, cm ³ mol ⁻¹	$-\Delta H_{r-n}$, kJ mol ⁻¹
2 + cycloheptatriene, ene synthesis	$6.12 \cdot 10^{-5}$	47.4	167	38.1/27.6 = 1.38	–
2 + cyclopentadiene [6], Diels–Alder reaction	$3.03 \cdot 10^{-3}$	33.8	180	44.5/35.8 = 1.24	112
1 + norbornene [17], ene synthesis with rearrangement	$1.28 \cdot 10^{-4}$	55.3	134	26.6/24.6 = 1.08	170 ^a
1 + norbornadiene [7], [2+2+2]-cycloaddition	$3.95 \cdot 10^{-3}$	50.9	120	25.1/31.0 = 0.81	218
1 + anthracene [7], Diels–Alder reaction	0.33	43.1	109	–	96.7
1 + 9,10-diphenylanthracene [18], Diels–Alder reaction at positions 1,4	$2.72 \cdot 10^{-3}$	58.6	97	17.2/15.6 = 1.10	50.2
1 + cyclohexene [19], ene synthesis	$8.07 \cdot 10^{-3}$	53.3	106	29.1/25.0 = 1.16	156
1 + 1-hexene [19], ene synthesis	$2.35 \cdot 10^{-3}$	51.8	122	31.0/26.6 = 1.16	158
1 + 2,3-dimethylbut-2-ene [19], ene synthesis	55.6	20 ^b	144	–	150

^a In 1,2-dichloroethane.

^b In benzene.

[6] the rate constant of the reaction of cycloheptatriene and compound **2** should be $\sim 1.4 \times 10^{-7}$ L mol⁻¹ s⁻¹. As follows from the data obtained (see the table) the rate of another reaction path, namely, of the ene synthesis between cycloheptatriene and compound **2**, is over 100 times faster than the Diels–Alder reaction. On the completion of the reaction between equimolar solutions of reagents **2** and **3** in the ¹H spectrum totally corresponding to that formerly described for adduct **4** [11] trace signals were detected of the Diels–Alder adduct **5**. After keeping the equimolar mixture of reagents **2** and **3** without solvent at 2 kbar for 50 h the fraction of the resonance signals of adduct **5** grew to 4%. At a higher hydrostatic pressure the fraction of adduct **5** grew even stronger [11]. Presumably, the change in the selectivity of the reaction and **2** + **3** → **4** + **5** at higher pressure is caused by the higher negative value of the activation volume of the Diels–Alder reaction **2** + **3** → **5** compared with the ene reaction **2** + **3** → **4**. The cyclic structures are known to be more compact than acyclic ones [20], therefore the volume of the activated complex in the ene reaction **2** + **3** → **4** which is less by 10.5 cm³ mol⁻¹ than the volume of adduct **4** should be ascribed to a cyclic form of the transition state whereas the product **4** proper is acyclic.

The variation of solution density was monitored with a precision densimeter DSA-5000M.

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