

## Kinetic and equilibrium parameters of [4+2] cycloaddition reaction of 2,6-dimethylnaphthalene with 4-phenyl-1,2,4-triazoline-3,5-dione

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Kinetic parameters of forward and retro Diels–Alder reactions between 2,6-dimethylnaphthalene and 4-phenyl-1,2,4-triazolinedione were determined, as well as the equilibrium parameters of the reaction in 1,2-dichloroethane.

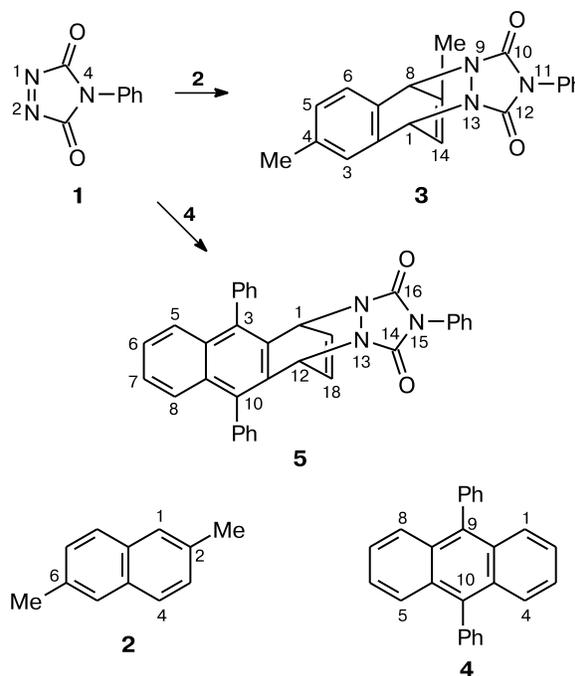
**Key words:** 2,6-dimethylnaphthalene, 4-phenyl-1,2,4-triazolinedione, Diels–Alder reaction, reaction rate, equilibrium.

In the sequence of aromatic dienes: benzene, naphthalene, anthracene, only the latter can be relatively easily involved in the Diels–Alder reaction with dienophiles.<sup>1</sup> Benzene fails to give this reaction due to the extremely unfavorable kinetic and equilibrium parameters. The reaction adduct between *N*-phenylmaleimide and naphthalene was obtained earlier by gallium chloride catalysis,<sup>2</sup> as well as under high pressure, which allowed to use elevated temperature.<sup>2,3</sup> The N=N bond in 4-phenyl-1,2,4-triazoline-3,5-dione is more active by almost five orders of magnitude in the Diels–Alder reaction than the C=C bond in the structural analog, *N*-phenylmaleimide, that allows one to obtain data on kinetic and equilibrium parameters of the Diels–Alder reaction even with low active dienes.<sup>4</sup> We have obtained kinetic and equilibrium parameters for the Diels–Alder reaction between 4-phenyl-1,2,4-triazoline-3,5-dione (**1**) and 2,6-dimethylnaphthalene (**2**) in 1,2-dichloroethane (Scheme 1). Recently, it was shown<sup>5</sup> that the active 9,10-reaction center in 9,10-diphenylanthracene **4** is completely blocked because of orthogonality of the anthracene plane and the plane of phenyl groups, that excludes a possibility of reaction with all known dienophiles with the C=C-reaction center.

Dienophile **1** was found to react with diene **4** at the sterically available 1,4-atoms of this diene.<sup>5</sup> It was interesting to compare kinetic and equilibrium parameters of the cycloaddition reactions of 4-phenyl-1,2,4-triazoline-3,5-dione at atoms C(1) and C(4) of dienes **2** and **4**.

The equilibrium constants obtained for the reaction  $\mathbf{1} + \mathbf{2} \rightleftharpoons \mathbf{3}$  are equal to 11.15, 8.40, and 4.48 L mol<sup>-1</sup> at 20.0, 25.0, and 35.0 °C, respectively. The calculated enthalpy and entropy values of the reaction are

Scheme 1



–44.0±2 kJ mol<sup>-1</sup> and –130±6 J mol<sup>-1</sup> K<sup>-1</sup>, respectively. The rate constants of the forward reaction  $\mathbf{1} + \mathbf{2} \rightarrow \mathbf{3}$  are equal to 3.26 · 10<sup>-4</sup>, 4.41 · 10<sup>-4</sup>, and 8.25 · 10<sup>-4</sup> L mol<sup>-1</sup> s<sup>-1</sup> at 20.0, 25.0, and 35.0 °C, respectively. From these data, the activation enthalpy (44.2±4 kJ mol<sup>-1</sup>) and entropy (–161±13 J mol<sup>-1</sup> K<sup>-1</sup>) were calculated. The rate constants of the adduct **3** decomposition ( $\mathbf{3} \rightarrow \mathbf{1} + \mathbf{2}$ ), calcu-

lated from the relation of the rate constants of the forward reaction  $\mathbf{1} + \mathbf{2} \rightarrow \mathbf{3}$  and the equilibrium constants, are equal to  $2.92 \cdot 10^{-5}$ ,  $5.07 \cdot 10^{-5}$ , and  $17.6 \cdot 10^{-5} \text{ s}^{-1}$  at 20.0, 25.0, and 35.0 °C, respectively. The activation enthalpy and entropy of the process  $\mathbf{3} \rightarrow \mathbf{1} + \mathbf{2}$  are  $88.2 \pm 4 \text{ kJ mol}^{-1}$  and  $-31 \pm 13 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively.

For the reaction  $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{5}$ , where addition takes place at atoms C(1) and C(4) of diene  $\mathbf{4}$ , the following rate constants in toluene were obtained:  $2.72 \cdot 10^{-3}$ ,  $5.73 \cdot 10^{-3}$ , and  $12.5 \cdot 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$  at 25, 35, and 45 °C, respectively. The rate constants of decomposition of adduct  $\mathbf{5} \rightarrow \mathbf{1} + \mathbf{4}$  for these temperatures are equal to  $1.29 \cdot 10^{-6}$ ,  $5.12 \cdot 10^{-6}$ , and  $23.4 \cdot 10^{-6} \text{ s}^{-1}$ , respectively. The calculated enthalpy and entropy of activation for the reaction  $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{5}$  are equal to  $58.6 \text{ kJ mol}^{-1}$  and  $-97 \text{ J mol}^{-1} \text{ K}^{-1}$ , whereas for the reaction  $\mathbf{5} \rightarrow \mathbf{1} + \mathbf{4}$  to  $108.8 \text{ kJ mol}^{-1}$  and  $7 \text{ J mol}^{-1} \text{ K}^{-1}$ . From this it follows that the enthalpy ( $-50.2 \text{ kJ mol}^{-1}$ ) and the entropy ( $-104 \text{ J mol}^{-1} \text{ K}^{-1}$ ) for the reaction  $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{5}$  are close to the corresponding parameters for the reaction  $\mathbf{1} + \mathbf{2} \rightarrow \mathbf{3}$ .

Earlier, it has been shown<sup>4</sup> that the enthalpy in the Diels–Alder reaction with dienophile  $\mathbf{1}$  and 4-phenylmaleimide is virtually the same. The enthalpy of the reaction  $\mathbf{1} + \mathbf{2} \rightarrow \mathbf{3}$  determined in the present work ( $-44.0 \text{ kJ mol}^{-1}$ ) is close to the value calculated earlier<sup>1</sup> ( $-43 \pm 4 \text{ kJ mol}^{-1}$ ) based on the heat of 1,4-dihydrogenation of the diene.

In conclusion, extremely high activity of 4-phenyl-1,2,4-triazoline-3,5-dione allowed us to determine kinetic and thermodynamic parameters in the Diels–Alder reaction with strongly conjugated and low active diene, *viz.*, 2,6-dimethylnaphthalene.

### Experimental

Dienophile  $\mathbf{1}$  (Aldrich, 97%) was sublimed at 100 °C and 10 Pa; m.p. 180 °C (decomp.),  $\lambda_{\text{max}}$ (benzene) = 540 nm ( $\epsilon$  248),  $\lambda_{\text{max}}$ (dioxane) = 527 nm ( $\epsilon$  186). Dienes  $\mathbf{2}$  and  $\mathbf{4}$  (Aldrich, 99%) were used without additional purification. Product  $\mathbf{5}$  was obtained according to the procedure described earlier.<sup>5</sup> Physicochemical and spectral characteristics agreed with those given in work.<sup>5</sup>

**(1R,8S)-4,15-Dimethyl-11-phenyl-9,11,13-triazatetracyclo[6.5.2.0<sup>2,7</sup>.0<sup>9,13</sup>]pentadeca-2,4,6,14-tetraene-10,12-dione ( $\mathbf{3}$ ).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), 25 °C,  $\delta_{\text{H}}$ : 7.20–7.60, 6.29 (d, quint, 1 H,  $J = 5.8 \text{ Hz}$ ,  $J = 1.8 \text{ Hz}$ ); 5.67 (d, 1 H,  $J = 5.8 \text{ Hz}$ ); 5.50 (d, 1 H,  $J = 1.8 \text{ Hz}$ ); 2.21 (s, 3 H); 1.89 (d, 3 H,  $J = 1.9 \text{ Hz}$ ).

The data completely agree with the structure of adduct  $\mathbf{3}$  and are close to the data for the adduct of the reaction of  $\mathbf{2}$  with 4-methyltriazolinedione.<sup>6</sup>

Solvents were dried using standard procedures.<sup>7</sup> Since reagent  $\mathbf{1}$  is sensitive to moisture, the constancy of optical density of solutions in time was controlled before kinetic measurements. Kinetic measurements were carried out under pseudo first order conditions on a HITACHI U-2900 spectrophotometer. Initial concentrations of reagents:  $C_2 = 0.17\text{--}0.21 \text{ mol L}^{-1}$ ,  $C_1 = (5.9\text{--}7.2) \cdot 10^{-3} \text{ mol L}^{-1}$ . The constancy of residual absorption of  $\mathbf{1}$  with time was a criterion of a steady-state equilibrium. The equilibrium was set up within 25 h. The course of the forward reaction was monitored based on the decrease in the absorption of  $\mathbf{1}$  in 1,2-dichloroethane,  $\lambda_{\text{max}} = 540 \text{ nm}$  ( $\epsilon$  178), where compounds  $\mathbf{2}$  and  $\mathbf{3}$  are transparent. Kinetic measurements for the reaction  $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{5}$  in toluene were carried out similarly. The rate of the retro reaction  $\mathbf{5} \rightarrow \mathbf{1} + \mathbf{4}$  was studied under conditions excluding equilibrium. For this, decomposition of adduct  $\mathbf{5}$  was carried out in the presence of *trans,trans*-1,4-diphenylbuta-1,3-diene, which rapidly and irreversibly caught dienophile  $\mathbf{1}$  formed upon decomposition of adduct  $\mathbf{5}$ . The reaction rate was monitored based on the increase in the absorption of diene  $\mathbf{4}$  on the 395 nm wavelength.

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