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Homo-Diels–Alder reaction of a very inactive diene, bicyclo[2,2,1]hepta-2,5-diene, with the most active dienophile, 4-phenyl-1,2,4-triazolin-3,5-dione. Solvent, temperature, and high pressure influence on the reaction rate

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Solvent, temperature, and high pressure influence on the rate constant of homo-Diels–Alder cycloaddition reactions of the very active hetero-dienophile, 4-phenyl-1,2,4-triazolin-3,5-dione (1), with the very inactive unconjugated diene, bicyclo[2,2,1]hepta-2,5-diene (2), and of 1 with some substituted anthracenes have been studied. The rate constants change amounts to about seven orders of magnitude: from $3.95\cdot10^{-3}$ for reaction (1+2) to 12200 L mol^{-1} s^{-1} for reaction of 1 with 9,10-dimethylanthracene (4e) in toluene solution at 298 K. A comparison of the reactivity (ln k_2) and the heat of reactions ($\Delta_{r\text{-}n}H$) of maleic anhydride, tetracyanoethylene and of 1 with several dienes has been performed. The heat of reaction (1+2) is -218 ± 2 kJ mol^{-1}, of 1 with 9,10-dimethylanthracene -117.8 ± 0.7 kJ mol^{-1}, and of 1 with 9,10-dimethoxyanthracene -91.6 ± 0.2 kJ mol^{-1}. From these data, it follows that the exothermicity of reaction (1+2) is higher than that with 1,3-butadiene. However, the heat of reaction of 9,10-dimethylanthracene with 1 (-117.8 kJ mol^{-1}) is nearly the same as that found for the reaction with the structural C=C counterpart, *N*-phenylmaleimide (-117.0 kJ mol^{-1}). Since the energy of the N=N bond is considerably lower (418 kJ/bond) than that of the C=C bond (611 kJ/bond), it was proposed that this difference in the bond energy can generate a lower barrier of activation in the Diels–Alder cycloaddition reaction with 1. Linear correlation ($R = 0.94$) of the solvent effect on the rate constants of reaction (1+2) and on the heat of solution of 1 has been observed. The ratio of the volume of activation ($\Delta V^{\neq}$) and the volume of reaction ($\Delta V_{r\text{-}n}$) of the homo-Diels–Alder reaction (1+2) is considered as "normal": $\Delta V^{\neq}/\Delta V_{r\text{-}n} = -25.1/-30.95 = 0.81$. **Copyright © 2012 John Wiley & Sons, Ltd.**

Keywords: activation volume; bicyclo[2,2,1]hepta-2,5-diene; heat of reaction; homo-Diels–Alder reaction; rate constants; reaction volume; 4-phenyl-1,2,4-triazolin-3,5-dione

INTRODUCTION

Norbornadiene or bicyclo[2,2,1]hepta-2,5-diene (**2**) is not a conjugated 1,3-diene, but can enter into a ($^2\pi+^2\pi+^2\pi$) homo-Diels–Alder cycloaddition reactions with some active dienophiles. The rate constants of Diels–Alder reactions with common electronic demand "diene-donor + dienophile-acceptor" can be estimated for reactants with C=C bonds using values of the ionization potential of the diene (IP), the electron affinity of the dienophile (EA), and the energy balance of breaking and forming bonds, reflected in the value of the enthalpy of reaction ($\Delta_{r\text{-}n}H$), and taking into account the interatomic distance in the diene, $R_{C(1)\text{-}C(4)}$, conditioning the degree of overlap of the reaction orbitals.[1,2] From this analysis, it follows that the influence of the energy of stabilization by orbital interactions on the change of reaction rates is about 50%, the influence of the enthalpy of reaction and the interatomic distance in the diene is about 25 % from the total energy change. Taking into account the values of the IP of bicyclo-2,5-heptadiene (8.69 eV)[3] and 1,3-butadiene (9.03 eV), [2] the interatomic distance in diene **2** ($R_{C(2)\text{-}C(6)} = 246$ pm),[4] and 1,3-butadiene ($R_{C(1)\text{-}C(4)} = 290$ pm),[2] the enthalpies of Diels–Alder reactions of 4-phenyl-1,2,4-triazolin-3,5-dione with bicyclo[2,2,1]hepta-2,5-diene (**2**) (-218 kJ mol^{-1}, this work) and with 1,3-butadiene (-189 kJ mol^{-1}), [5] one can expect a much higher activity of diene **2** in comparison with 1,3-butadiene. The rate constants of the reaction of diene **2** with 4-phenyl-1,2,4-triazolin-3,5-dione (**1**) and with tetracyanoethylene (**6**) do not meet these expectations (Table 1). Bicyclo[2,2,1]hepta-2,5-diene (**2**) is about three orders of magnitude less active in homo-Diels–Alder reaction than 1,3-butadiene in Diels–Alder reactions with the same dienophiles.

One of the reasons for the low reactivity of homo-diene **2** in homo-Diels–Alder reaction can be the difficulty of a concerted formation of the new C_3–C_5 cyclopropane bond in adduct **3**. This

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Table 1. Rate constants (k_2/L mol^{-1} s^{-1}) and enthalpies ($\Delta_{r\text{-}n}H$/kJ mol^{-1}) of Diels–Alder cycloaddition reactions of some dienes with maleic anhydride, tetracyanoethylene, and 4-phenyl-1,2,4-triazolin-3,5-dione at 298 K

Dienes	Maleic anhydride		Tetracyanoethylene		4-Phenyl-1,2,4-triazolin-3,5-dione	
	k_2	$-\Delta_{r\text{-}n}H$	k_2	$-\Delta_{r\text{-}n}H$	k_2	$-\Delta_{r\text{-}n}H$
9-Chloro-anthracene	$1.23\cdot10^{-6}$, S-1 [6] $1.43\cdot10^{-6}$, S-2 [7]	82[a], S-1, [2]	0.70, S-2 [8]	66.1, S-2 [9]	0.130, S-3 [b] 0.180, S-4 [5]	72.8, S-4, 303 K [5];
Anthracene	$5.25\cdot10^{-6}$, S-1 [6] $6.01\cdot10^{-6}$, S-2 [7]	93[a], S-1 [2]	5.47, S-5 [10]; 0.010, S-7 [11]; 3.82, S-2 [11] [c]	76.6, S-2 [9]; 77, S-1 [9]	0.028, S-6 [12]; 0.13, S-1, 303 K [13]; 0.33, S-3 [b]	96.7, S-4, 303 K [5]
9-Methyl-anthracene	$3.09\cdot10^{-4}$, S-1 [6]; $3.45\cdot10^{-4}$, S-2 [7]	101[a], S-1 [2]	2230, S-2 [9]	84.5, S-2 [9]; 85.0, S-1 [9]	84.0, S-3 [b]	101.9, S-4, 303 K [5];
9-Phenyl-anthracene	$3.6\cdot10^{-7}$, S-3 [14]	81, S-8 [15]	No data	n/d	0.4, S-3 [b]	72.2, S-3 [b]
9-Methoxy-anthracene	$2.5\cdot10^{-5}$, S-1 [6]; $2.84\cdot10^{-5}$, S-2 [7]	77[a], S-1 [2]	5170, S-2 [9]	61.1, S-1 [9]	n/d	93.5, S-4, 303 K [5];
9,10-Dimethyl-anthracene	0.0122, S-2 [7]; 0.07, S-5 [10]; 0.012, S-1 [16]c	104, S-1 [2]	89000, S-2 [17]; 220000, S-5 [17]c	88.3, S-2 [9]; 90.4, S-1 [9]	12180, S-3 [b]	117.8, S-2 [b]
9,10-Dimethoxy-anthracene	$2.8\cdot10^{-6}$, S-1 [6]; $3.11\cdot10^{-6}$, S-2 [7]	69[a], S-1 [2]	870, S-2 [9]; 370, S-9 [9]	51.5, S-1 [9]	13750, S-3 [b]	91.6,S-2 [b]
Norbornadiene	n/d	196 S-2 [a,d]	$1.3\cdot10^{-5}$, S-3, 308 K [10]c $3.0\cdot10^{-5}$, S-4, 308 K [10]c	180 S-2 [a]	$3.95\cdot10^{-3}$, S-3 [b] $9.4\cdot10^{-3}$, S-4, 303 K [13]c	218.0, S-3 [b]
1,3-Butadiene	$6.76\cdot10^{-5}$, S-1 [2]	170 [a], S-1 [2]	$1.7\cdot10^{-3}$, S-2 [2]	154, S-10, [2]	6.92, S-4 [5]	201, S-4 [5]
2-Methyl-butadiene	$1.55\cdot10^{-4}$, S-1 [2]	182[a], S-1 [2]	$7.41\cdot10^{-2}$, S-2 [2]	166, S-10, [18]	46, S-4 [5]	217, S-4 [5]
2,3-Dimethyl-butadiene	$3.39\cdot10^{-4}$, S-1 [2]	194[a], S-1 [2]	2.51, S-2 [2]	178, S-10 [19]	180, S-4 [5]	218, S-4 [5]
trans-1-Phenyl-butadiene	$1.12\cdot10^{-4}$, S-1 [2]	158[a], S-1 [2]	0.646, S-2 [2]	142, S-10 [2]	63.1, S-4 [5]	186, S-4 [5]
trans, *trans*-1,4-Diphenylbutadiene	$2.95\cdot10^{-6}$, S-1 [2]	113[a], S-1 [2]	$7.41\cdot10^{-2}$, S-2 [2]	97, S-10 [2]	1.10, S-4, 293 K [20] 6.19, S-4, 303 K [13] 51.9, S-5 [12]c	142, S-4 [5]
Cyclopentadiene	$9.12\cdot10^{-2}$, S-1 [2]	129, S-1 [2]	478, S-1 [2]	113, S-10 [2]	n/d	134, S-4 [5]
Hexachloro-cyclopentadiene	$1.15\cdot10^{-8}$, S-1 [2]	58[a], S-1 [2]	n/d	42[a], S-10 [2]	$4.34\cdot10^{-3}$, S-4, 323 K [13] $17.5\cdot10^{-5}$, S-11 [21]c	77, S-4 [5]

[a]Calculated from equation: $\Delta_{r\text{-}n}H$ (D$_1$ + A$_1$) - $\Delta_{r\text{-}n}H$ (D$_1$ + A$_2$) = $\Delta_{r\text{-}n}H$ (D$_2$ + A$_1$) - $\Delta_{r\text{-}n}H$ (D$_2$ + A$_2$), where D and A are dienes and dienophiles. Unknown values for the enthalpy of slow reactions can be estimated from three values of enthalpies of three other reactions, which are convenient for calorimetric measurements.
[b]This work.
[c]In these works, the rate constants were determined in the range of solvents. Solvent abbreviations: S-1, 1,4-dioxane; S-2, 1,2-dichloroethane; S-3, toluene; S-4, benzene; S-5, trichloromethane; S-6, tetrahydrofuran; S-7, mesitylene; S-8, 1,2-dichlorobenzene; S-9, acetonitrile; S-10, dichloromethane; S-11, ethyl acetate.

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bond forms in homo-Diels–Alder reaction (**1**+**2**) from the large distance (246 pm), almost on 100 pm longer than C_2–C_3 in the diene moiety of the activated complex of common Diels–Alder reactions. At the present time, the rate constant of reaction **2** with maleic anhydride (**10**) is still unknown.

4-Phenyl-1,2,4-triazolin-3,5-dione (**1**), is a heteroatomic dienophile in the studied homo-Diels–Alder reaction, with a N=N reaction centre instead of the common C=C bond. With various dienes collected in Table 1, dienophile **1** has an unusually high reactivity, exceeding tetracyanoethylene by two orders of magnitude. Tetracyanoethylene (**6**) (EA = 2.88 eV) is the most active π-acceptor dienophile in Diels–Alder reactions only with the strong π-donor dienes, i.e. with anthracene and its substituted derivatives. Extensive data on the reaction rates of 4-substituted-1,2,4-triazolin-3,5-diones with several dienes in different solvents have been reported, [12,13,20], but the reasons of the unusually high reactivity of **1** have not been clarified yet. A simple linear relation, ln $(k_2/k_1) = 8.3 - 0.85IP$, was observed between IP and the rate constants of 4-(4-nitrophenyl)-1,2,4-triazolin-3,5-dione (k_2) and 4-phenyl-1,2,4-triazolin-3,5-dione (k_1) with several dienes, [13] indicating on the π-acceptor type of **1**.

In this work, the solvent, temperatures, and pressure influence on the rate of the homo-Diels–Alder reaction of 4-phenyl-1,2,4-triazolin-3,5-dione (**1**) with bicyclo[2,2,1]hepta-2,5-diene (**2**) have been studied. The rate and the heat of reactions of some dienes with **1** have also been measured. The values of enthalpy, entropy, and volume of activation, the volume and enthalpy of reactions, as well as the heats of solution of **1**,**7–9** in some solvents have been also obtained (Scheme 1_).

EXPERIMENTAL

Materials

Bicyclo[2,2,1]hepta-2,5-diene (Alfa Aesar, England, 97%) was distilled immediately before measurements: b. p. 362.5-363.5 K, n_{20} =1.4702. 4-Phenyl-1,2,4-triazolin-3,5-dione (Aldrich, Germany, 97%) was sublimed before the measurements at 373 K and 100 Pa. The spectral purity of **1** was analyzed by the known absorption coefficient ($\varepsilon_{532\ nm}$ is 171 in 1,4-dioxane at 298 K). [20] Dienes **4a–g** were prepared and purified as described before. [9] All solvents were purified and dried by known methods. [22]

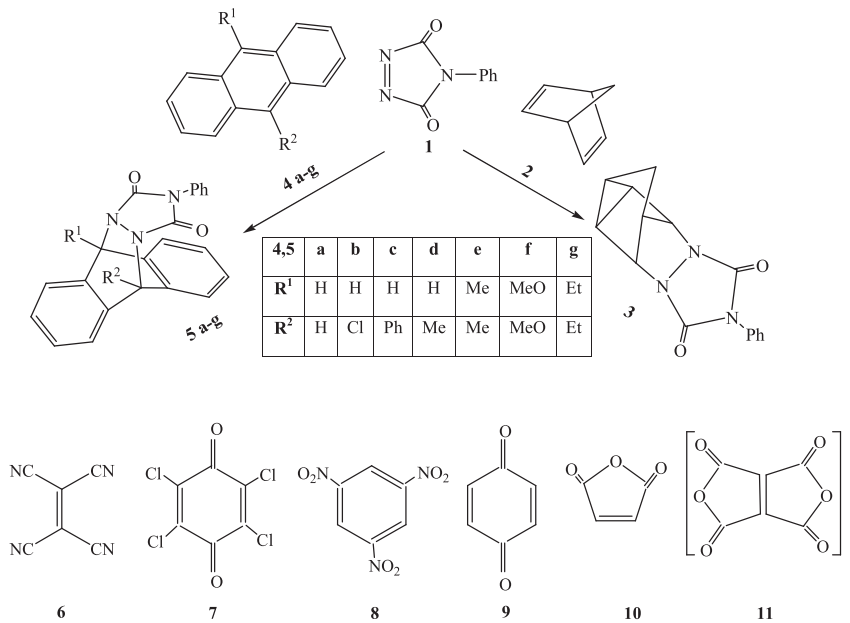
Kinetic measurements

The rate of reaction (**1+2**) was determined by measuring the UV absorption of dienophile **1** at 540 nm (ε_{540} equal 247 in toluene at 298 K). The initial concentration of dienophile **1** was in the range $(3–5)\cdot10^{-3}$ mol L^{-1} and that of diene **2** $(1–2)\cdot10^{-1}$ mol L^{-1}. Diene **2** and adduct **3** are transparent in this range of spectra. The water-circulating cell-holder adapter (type 210-2111) of the UV-spectrophotometer Hitachi-2900 with only one-side T-control was removed and replaced by the new five-side T-control in a water circulating box, which allowed an accuracy of ±0.1 K. The rate constants of reactions **1** with **4c** were measured under similar conditions, and with dienes **4a** and **4b**, the initial concentrations of both reactants were equal $(2–4)\cdot10^{-3}$ mol L^{-1}. Very fast reactions of **1** with **4d–4g** were measured by the stopped-flow method (RX 2000 with spectrophotometer Cary 50 Bio) in toluene solution at 298 K by monitoring the absorption of dienes **4d–4g** in the range 390–405 nm ($\varepsilon = 5\cdot10^3 - 2\cdot10^4$ L mol^{-1} cm^{-1}). The initial concentration of **1** was about $1\cdot10^{-3}$ mol L^{-1}, and the concentration of dienes **4d–4g** was about $1\cdot10^{-4}$ mol L^{-1}. The values of the rate constants were determined with errors of ±3%, the enthalpy of activation of ±2 kJ mol^{-1}, and the entropy of activation of ±6 J mol^{-1} K^{-1}.

The rate constants of reaction (**1**+**2**) under elevated pressure were measured in toluene solution at 298 K with the high pressure system using the high pressure pump "HP-500" and high pressure optical cell "PCI-500" from Syn. Co., Ltd (Japan), adjusted to a UV-spectrophotometer from SCINCO Co., Ltd (Korea). The photodiode array of the "SCINCO" UV-spectrophotometer performs all new spectra in the selected time interval.

Calorimetry

The enthalpies of solution of reactants **1** and **7–9** were measured at 298 K with a differential calorimeter, as previously reported. [16,23] Samples were weighed into a small stainless-steel cylinder, both polished sides of which were covered by thin (0.1 mm) rings of Teflon seals and sealed by a screwed cap. The mass of the cylinders filled with diethyl ether



4,5	a	b	c	d	e	f	g
R^1	H	H	H	H	Me	MeO	Et
R^2	H	Cl	Ph	Me	Me	MeO	Et

Scheme 1. (^{4}pi+^{2}pi) Diels-Alder reaction of 4-phenyl-1,2,4-triazolin-3,5-dione (**1**) with substituted anthracenes (**4a–g**) and (^{2}pi+^{2}pi+^{2}pi) homo-Diels-Alder cycloaddition of **1** with norbornadiene (2), and some pi-acceptor compounds (**6–11**)

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proved to be constant after 24 h, ensuring the tightness of the container. After equilibrium of temperature, these Teflon seals were cut out by a razor. The accuracy of the calorimetric measurements was verified by determining the enthalpy of dissolution of dry potassium chloride in water at 298 K. The result (17.4 ± 0.2 kJ mol^{-1}) is in agreement with the published value of (17.514 ± 0.008 kJ mol^{-1}).[24] For all solutions, 3–5 measurements of sequentially dissolving samples were carried out. The total uncertainty of the measurements did not exceed ±2%. No concentration dependences of the heat of solution were observed.

The heat of reaction (**1**+**2**) was measured by addition of solid **1** (25–35 mg) to a toluene solution of diene **2** (1.5–2.0 mol L^{-1}), and for reactions (**1**+**4e**) and (**1**+**4f**) by addition of 35–45 mg of solid **1** to a 1,2-dichloroethane solution of diene (10^{-2} mol L^{-1}). The values of enthalpies of reactions were calculated taking into account the heat of solution of solid **1** in toluene (18.3 kJ mol^{-1}) and in 1,2-dichloroethane (21.9 kJ mol^{-1}).

Volume parameters

The volume of activation, $\Delta V^{\neq}$, was calculated from the dependence $\ln k_p$ versus P, were k_p is the rate constant of reaction (**1**+**2**) under pressure P. The reaction volume is usually calculated by the difference of the partial molar volumes (PMV) of adduct and reactants with a total error of ±1–2 cm^{3}mol^{-1}. This error can be sharply decreased using a kinetic method. The vibration densimeter manufactured by Anton Paar, model DSA 5000 M, was used for the measurements at 298 ± 0.002 K. The densimeter was calibrated with water and air following the instructions.

RESULTS AND DISCUSSIONS

Kinetic measurements at ambient pressure

The cause of epy outrageously high reactivity of dienophile **1** is still unknown.[12,13,20] The very high reactivity of tetracyanoethylene (**6**)[9,10,17] and of the dianhydride of ethylenetetracarbonic acid (**11**)[25–27] as dienophiles in Diels–Alder reactions, conditioned by the high value of π-EA of **6** (EA = 2.88 eV), and the high strain energy of the C=C bond in dienophile **11**. All efforts to isolate the compound **11** have failed.[25–27] In this work, it was assumed that the range of π-acceptor properties can be estimated by the difference of the heat of solution in π-donor solvents, e.g. in substituted benzenes. The data obtained were collected in Table 2.

As it follows from Fig. 1, the changes of the heat of solution of the π-acceptors studied in π-donor solvents arrange the acceptor properties in the following sequence: tetracyanoethylene (**6**), 100%, blank, correlation coefficient, $r = 1$; tetrachloro-1,4-benzoquinone (**7**), 43%, $r = 0.97$; 1,3,5-trinitrobenzene (**8**), 24%, $r = 0.99$; 4-phenyl-1,2,4-triazolin-3,5-dione (**1**), 19%, $r = 0.94$; maleic anhydride (**10**), 15%, $r = 0.99$); 1,4-benzoquinone (**9**), 6%, $r = 0.95$.

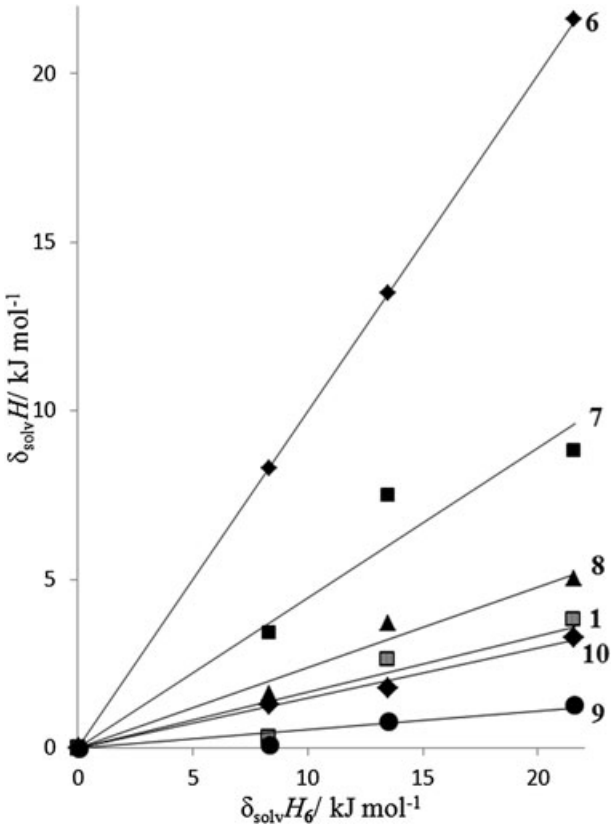

Figure 1. Linear correlations of the enthalpy of solvation of tetracyanoethylene (**6**) ($\delta_{solv}H_6 = \Delta_{sol}H_6$ (S_l) - $\Delta_{sol}H_6$ (*o*-xylene) with that of tetrachloro-1,4-benzoquinone (**7**), 1,3,5-trinitrobenzene (**8**), 4-phenyl-1,2,4-triazolin-3,5-dione (**1**), maleic anhydride (**10**), 1,4-benzoquinone (**9**)

In addition, the influence of π-donor solvents on the rate constants (Table 2) comes in a similar order: tetracyanoethylene, 100%, blank, $r = 1$; 4-phenyl-1,2,4-triazolin-3,5-dione, 45%, $r = 0.997$; maleic anhydride, 34%, $r = 0.967$). This means that the acceptor properties of dienophiles **1** and **10** are moderate and

Table 2. Enthalpies of solution ($\Delta_{sol}H$/kJ mol^{-1}) of some π-acceptors and the rate constants (k_2/L mol^{-1} s^{-1}) of the Diels–Alder reactions in π-donor solvents at 298 K

π-Acceptor	*o*-Xylene		Toluene		Benzene		Chlorobenzene	
	$\Delta_{sol}H$	k_2	$\Delta_{sol}H$	k_2	$\Delta_{sol}H$	k_2	$\Delta_{sol}H$	k_2
Tetracyanoethylene	1.4	0.061[a]	9.7	0.13[a]	14.9	0.38[a]	23.0	1.82[a]
Tetrachloro-1,4-benzoquinone	9.2	–	12.6	–	16.7	–	18.0	–
s-Trinitrobenzene	5.9	–	7.5	–	9.6	–	10.9	–
4-Phenyl-1,2,4-triazolin-3,5-dione	18.0	0.21[b]	18.3	0.33[b]	20.6	0.52[b]	21.8	1.01[b]
Maleic anhydride	15.1	0.017[c]	16.4	0.019[d]	16.9	0.022[d]	18.4	0.045[d]
1,4-Benzoquinone	16.3	–	16.4	–	17.1		17.6	–

[a]With anthracene, Ref. [10,11].
[b]With anthracene, Ref. [12].
[c]This work.
[d]With 9,10-dimethylanthracene, Ref. [16].

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rather similar, and they cannot be the reason of the very high differences in reactivity {log (k_1/k_{10}) ≈ 4–6, Table 1}. Note, that in the Diels–Alder reactions with moderate π-donor dienes, e.g. substituted butadiene, 4-phenyl-1,2,4-triazolin-3,5-dione is more active than tetracyanoethylene (Table 1).

The solvent influence on the heat of solution of reactants **1** and **4a** as well as on the rate of the Diels–Alder reaction (**1**+**4a**) is collected in Table 3.

The solvent effect on the rate constant was studied for the reaction of **1** with 1,2,3,4-tetrachlorocyclopentadiene, [21] and turned out to be very similar to that in the reaction (**1**+**4a**), Table 3, (r = 0.987, n = 9, slope 0.925). A comparison of the solvent effect on the rate (ln k_2) and the heat of solution of diene ($\Delta_{sol}H_{4a}$) leads to the conclusion that the differences in diene **4a** solvation do not influence the reaction rate at all (r = 0.15). This is unlike the differences of the dienophile (**1**) solvation, where a linear correlation (r = 0.94, n = 12) of ln k_2 versus $\Delta_{sol}H_1$ was observed (Fig. 2).

It means that the changes in enthalpy of solvation of dienophile **1** ($\delta_{solv}H_1$) in the studied solvents differ sharply from the change of the dienophile **1** solvation in the activated complex. The same conclusion was made before in the reaction of maleic anhydride with 9,10-dimethylanthracene. [16] The most striking example was observed in the Diels–Alder reaction with tetracyanoethylene where the differences of the solvation of **6** are almost completely disappearing in the activated complex. [29]

Activation parameters of the homo-Diels–Alder reaction (**1**+**2**), (Table 4), are nearly the same as those for the Diels–Alder reaction (**1**+**4a**), (Table 2).

In a polar solvent, such as acetonitrile, the rate constant is nearly the same as in toluene. The entropy of activation of reaction (**1**+**2**) should be more negative due to the shielding of one side of bicyclo-2,5-heptadiene **2** by the C_7 bridge.

The rate constants of reaction (**1**+**4a**) in different solvents are collected in Table 3. Very fast reaction rates with $t_{1/2}$ <1 s were measured by the stopped flow method in toluene at 298 K (Table 1).The mean values of the rate constants are for reaction (**1**+**4d**), 84.0 ± 0.6 L mol^{-1} s^{-1} (nine doubles); for (**1**+**4e**), 12180 ± 140 L mol^{-1} s^{-1} (eight doubles); for (**1**+**4f**), 13750 ± 200 L mol^{-1} s^{-1} (eleven doubles); and for (**1**+**4g**), 828 ± 6 L mol^{-1} s^{-1} (13 doubles). Adducts of these reactions were analyzed before. [20] Steric hindrances in the reaction of 9,10-diethylanthracene **4g** with **1** reduce the rate constant by factor of 15, as compared with reaction (**1**+**4e**). Nearly the same ratio was observed in reactions (**4g**+**10**) and (**4e**+**10**). [6] A sharp decrease in reactivity

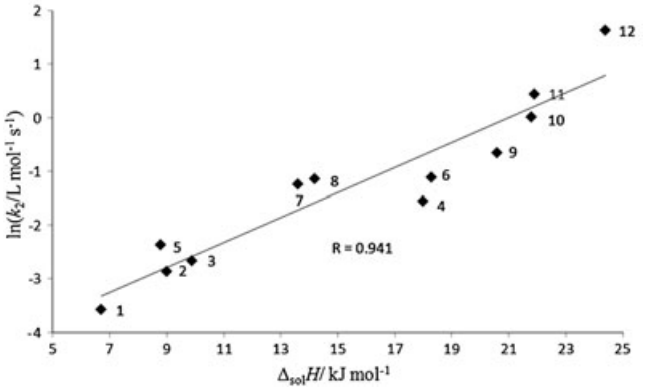

Figure 2. Linear correlation between the enthalpies of solution ($\Delta_{sol}H_1$) of 4-phenyl-1,2,4-triazolin-3,5-dione (**1**) in some solvents and the rate constants, (ln k_2) of reaction (**1**+**2**). The solvent numeration is as in Table 3

Table 4. 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 Gibbs energy ($\Delta G^{\neq}$/kJ mol^{-1}) of activation for the Diels–Alder reaction (**1**+**2**) in toluene

T/K	k_2	R	N	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
288	0.00180	0.99991	17	50.9	−120.5	86.8
298	0.00395	0.99996	17			
308	0.00763	0.99994	19			
298	0.00317[a]	0.99992[a]	16[a]	–	–	–

[a]In acetonitrile.

Table 3. Enthalpies of solution ($\Delta_{sol}H$/kJ mol^{-1}) of anthracene (**4a**) and 4-phenyl-1,2,4-triazolin-3,5-dione (**1**) as well as 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}), and Gibbs energies ($\Delta G^{\neq}$/kJ mol^{-1}) of activation of the Diels–Alder reaction, measured in twelve solvents at 298 K

No	Solvent	$\Delta_{sol}H_{4a}$ [a]	$\Delta_{sol}H_1$	k_2	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	$\Delta G^{\neq}$
1	Tetrahydrofuran	18.2	6.7	0.028	50.2	105	81.5
2	Ethyl acetate	25.1	9.0	0.057 [b]	48.5 [b]	106 [b]	80.1[b]
3	Methyl acetate	25.0	9.9	0.070	46.4	113	80.0
4	*o*-Xylene	24.0	18.0	0.21 [c]	46.0	105	77.3
5	1,4-Dioxane	22.6	8.8	0.094 [b]	43.9 [b]	117 [b]	78.8[b]
6	Toluene	24.8	18.3	0.33 [c]	43.1	109	75.6
7	Benzonitrile	25.6	13.6	0.29	41.8	117	76.6
8	Acetonitrile	28.0	14.2	0.32	38.5	125	75.8
9	Benzene	24.7	20.6	0.52 [c]; 0.50[b]	35.1	134	75.0
10	Chlorobenzene	24.6	21.8	1.01 [c]	31.8	138	72.9
11	1,2-Dichloroethane	24.9	21.9	1.55	28.0	146	71.5
12	Trichloromethane	20.8	24.4	5.09	23.4	155	69.6

[a]From Ref. [12,28].
[b]From Ref.[13].
[c]Ref [12].

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was observed for 9-phenylanthracene and, especially, for 9, 10-diphenylanthracene, due to the almost orthogonal orientation of the planes of anthracene and the phenyl moieties. [14]

Kinetic measurements at high pressure

The pressure influence on the rate constant of reaction (**1**+**2**) has been studied in toluene at 25 °C (Fig. 3, Table 5).

From the experimental dependence given by the equation: $\ln(k_p/k_{p=1}) = 1.098\cdot10^{-3}P - 7.679\cdot10^{-8}P^2$ ($r = 0.9995$, $n = 9$) follows that the apparent value of the volume of activation is −27.2 0.8 $cm^3\,mol^{-1}$. After correction because of the compressibility of the solvent ($RT\cdot\beta_{298}$, where β_{298} is the compressibility coefficient of toluene at 298 K, equal $90\cdot10^{-6}\,bar^{-1}$, [30]) the value of activation volume, $\Delta V^{\neq}$, is −25.1 ±0.8 $cm^3\,mol^{-1}$.

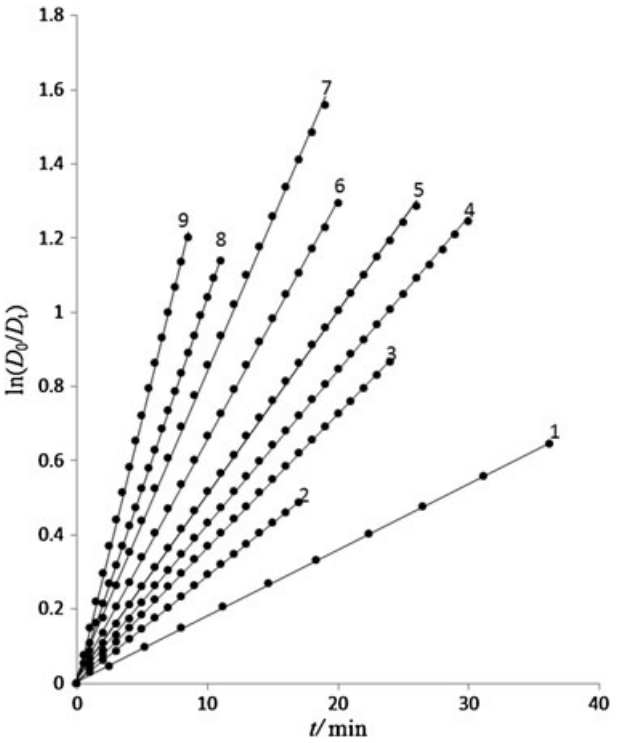

Figure 3. Anamorphosis of the kinetic runs of the homo-Diels–Alder reaction (**1**+**2**) in toluene solution under high pressure at 298 K: 1–1; 2–407; 3–616; 4–757; 5–945; 6–1215; 7–1538; 8–1748 and 9–2166 bar

Table 5. Pressure (P/bar) effect on the rate constant (k_2/L $mol^{-1}\,s^{-1}$) of the homo-Diels–Alder reaction of 4-phenyl-1,2,4-triazolin-3,5-dione with bicyclo[2,2,1]hepta-2, 5-diene, (**1**+**2**), measured in toluene at 298 K

P	$10^3\,k_p$	$\ln(k_p/k_{p=1})$
1	3.9	0
407	6.0	0.419
616	7.5	0.647
757	8.7	0.788
945	10.3	0.963
1215	13.5	1.230
1538	17.2	1.471
1748	21.6	1.701
2166	29.5	2.011

It is important to determine the ratio of the values of activation ($\Delta V^{\neq}$) and reaction ($\Delta V_{r\text{-}n}$) volumes, $\Delta V^{\neq}/\Delta V_{r\text{-}n}$. Here, we use the more accurate method of determination of $\Delta V_{r\text{-}n}$. The total volume of solution with reagents **1**, **2**, and adduct **3** can be written by Eqns (1) and (2):

$$V_{(t)} = V_s + (c^0_{\mathbf{1}} - c_{\mathbf{3},\,t})\cdot V_{\mathbf{1}} + (c^0_{\mathbf{2}} - c_{\mathbf{3},\,t})\cdot V_{\mathbf{2}} + c_{\mathbf{3},\,t}\cdot V_{\mathbf{3}} \quad (1)$$

$$V_{(t)} = \left[V_s + \left(c^0_{\mathbf{1}}\cdot V_{\mathbf{1}} + c^0_{\mathbf{2}}\cdot V_{\mathbf{2}}\right)\right] + c_{\mathbf{3},\,t}\cdot(V_{\mathbf{3}} - V_{\mathbf{1}} - V_{\mathbf{2}}) = V_{(t=0)} + c_{\mathbf{3},\,t}\cdot\Delta V_{r-n} \quad (2)$$

$$1/d_{(t)} = 1/d_{(t=0)} + c_{\mathbf{3},\,t}\cdot\Delta V_{r-n}/1000d_{(t=0)} \quad (3)$$

Equation (3), rewritten from Eqn (2), is more convenient for the density measurements 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 volume of solvent; $V_{\mathbf{1}}$, $V_{\mathbf{2}}$, and $V_{\mathbf{3}}$ are PMVs of compounds **1**, **2**, and **3**; $c^0_{\mathbf{1}}$, $c^0_{\mathbf{2}}$, and $c_{\mathbf{3},\,t}$ are the initial molar concentrations of **1** and **2**, and the current concentration of **3**; $\Delta V_{r\text{-}n}$ is the reaction volume. Linear dependences $1/d_{(t)}$ versus $c_{\mathbf{3}}$ (Fig. 4) were observed for two runs up to 95% conversion. The values of the reaction volume were calculated as −30.81 ± 0.08 and −31.09 ± 0.11 cm^3mol^{-1}. For the large part of the studied Diels–Alder reactions, a "normal" ratio, $\Delta V^{\neq}/\Delta V_{r\text{-}n}$ 1, was observed.[31–33] Such value is clear, taking into account the incomplete bond formations in the activated complex as compared with the adduct. However, for nearly the same number of Diels–Alder reactions, an "abnormal" ratio, $\Delta V^{\neq}/\Delta V_{r\text{-}n} > 1$, was observed. [31–33] For the studied homo-Diels–Alder reaction (**1**+**2**), the "normal" ratio $\Delta V^{\neq}/\Delta V_{r\text{-}n} = -25.1/-30.95 = 0.81$ is obtained. For reaction (**1**+**6**) in toluene at 298 K, nearly the same "normal" ratio $\Delta V^{\neq}/\Delta V_{r\text{-}n} = -28.1/-32.9 = 0.85$ was reported. [34]

Calorimetric data

Obtained values of enthalpies of solution of compounds **1, 7–9** are collected in Tables 2 and 3 and were already discussed above. The heat of reactions (**1**+**2**), (**1**+**4e**), and (**1**+**4f**) were measured by addition of 25–40 mg of solid **1** to a solution of dienes **2** (1.5 mol L^{-1} in toluene), to a solution of **4e** ($1\cdot10^{-3}$ mol·L^{-1} in toluene), and to a solution of **4f** ($2\cdot10^{-3}$ mol L^{-1} in 1,

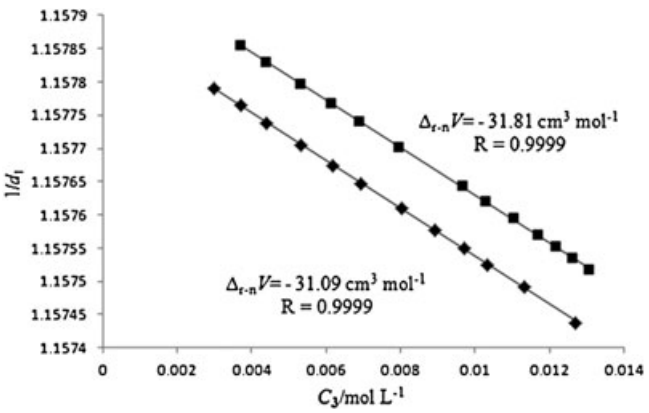

Figure 4. Relation between the specific volume ($1/d_t$) during the reaction of (**1**+**2**) in toluene solution and the concentration of adduct **3** ($C_{\mathbf{3}}$) at 298 K. For clarity, line (■) for repeated measurement was shifted up on $1\cdot10^{-4}$ unity of the ordinate scale

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2-dichloroethane). The heat of homo-cycloaddition (**1**+**2**) deserves particular attention. From three independent measurements of the heat of reaction (**1**+**2**) in toluene at 298 K, the following values were obtained: −219; −214, and −220 kJ mol^{-1}. The exothermicity of reaction (**1**+**2**) is -218 ± 2 kJ mol^{-1}, higher than that of **1** with substituted butadiene (Table 1). The values of the heats of reaction (**1**+**4e**) (−118.4, −116.7, and −118.3 kJ mol^{-1}) and (**1**+**4f**) (−91.66, − 91.75, and −91.29 kJ mol^{-1}) were also obtained. The linear relation between the values of the heat of reactions of the same dienes with 4-phenyl-1,2,4-triazolin-3, 5-dione and with tetracyanoethylene (Table 1) reflects the difference in the diene conjugation. From these data, it follows that the exothermicity of reactions of dienes with **1** is higher than that with **6**. However, it should be noted that the heat of reaction of 9,10-dimethylanthracene (**4e**) with 4-phenyl-1,2,4-triazolin-3,5-dione (-117.8 ± 0.7 kJ mol^{-1}) is nearly the same as in reaction of **4e** with the structural C=C counterpart, *N*-phenylmaleimide (−117 kJ mol^{-1}). [2] From these data, it can be concluded that the high exothermicity of the Diels–Alder reactions with 4-phenyl-1,2,4-triazolin-3,5-dione cannot be the determining factor of the very high reactivity of **1**.

CONCLUSIONS

Rate constants of the Diels–Alder cycloaddition reactions between reactants with C=C bonds can be satisfactorily predicted taking into account three main parameters:(i) the stabilization energy due to donor–acceptor intermolecular orbital interactions; (ii) the energy balance of breaking and forming bonds, and (iii) the interatomic distance between the reaction centers of the 1,3-diene (R_{1-4}). [2] Neither of these factors can explain the unusually low reactivity of bicyclo[2,2,1]hepta-2, 5-diene in the homo-($^2\pi + ^2\pi + ^2\pi$)-cycloaddition, which is similar to the ($^4\pi + ^2\pi$) Diels–Alder reaction, but still is another process, and the unusually high reactivity of the heterodienophile, 4-phenyl-1,2,4-triazolin-3,5-dione, with an N=N reaction centre. From the kinetic and calorimetric data obtained, it can be assumed that the very low activity of **2** in the cycloaddition reaction is caused by the difficulty to form the new C–C bond in the cyclopropane moiety in the activated complex. It is known that the energy of orbital interactions can only stabilize the activated complex and decrease the value of the activation barrier.[2] In the concerted Diels–Alder cycloaddition reaction, this barrier is created, in the first place, by the beginning of the partial breakage of π–π bonds with the following generation of new bonds. Since the energy of the N=N bond is considerably lower (418 kJ/bond) than that of the C=C bond (611 kJ/bond), [35] this difference in the energy of breaking bonds can generate a lower barrier of activation in the Diels–Alder cycloaddition reactions with **1**, in spite of nearly the same acceptor properties of **1** and maleic anhydride **10**, and the same values of the heat of reactions of the dienes with **1** and with **10**. The pressure influence on the rate constant of the homo-Diels–Alder reaction (**1**+**2**), its volume of activation, and its volume of reaction are similar to the "normal" ($^4\pi + ^2\pi$)-cycloaddition reaction. Thereby, an analysis of the reasons of the very low and very high reaction rates helps to understand the nature of reactivity of different systems in cycloaddition processes.

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