



Reactivity Variation of Tetracyanoethylene and 4-Phenyl-1,2,4-Triazoline-3,5-Dione in Cycloaddition Reactions in Solutions

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Received: 7 May 2018 / Accepted: 7 October 2018 / Published online: 22 January 2019
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Abstract

The reasons for the very high reactivity and variability of reactivity of two dienophiles, tetracyanoethylene (1) and 4-phenyl-1,2,4-triazoline-3,5-dione (2), in the Diels–Alder reactions were considered. The data on the rate of reactions with anthracene (3), benzanthracene (4) and dibenzanthracene (5) in 14 solvents over a range of temperatures and high pressures, data on the change in the enthalpy of solvation of reagents, transition state, and adducts in the forward and backward reactions, and the enthalpies of these reactions in solution were obtained. Strong π -acceptor dienophile 1 has sharply reduced reactivity in reactions in π -donor aromatic solvents. It was observed that the π -acceptor properties of dienophile 1 disappear upon passage to the transition state and adduct. Large solvent effects on the reaction rate can be predicted for all types of reactions involving tetracyanoethylene. Very high reactivity of dienophiles 1 and, especially, 2 can be useful to catch such carcinogenic impurities such as 3–5 and neutralize them by transformation into less dangerous adducts.

Keywords High pressure · Diels–Alder reaction · Kinetics · Transition state · Enthalpy

1 Introduction

An increased interest in the Diels–Alder reaction (DAR) is due to its enormous potential in laboratory and industrial synthesis of a variety of cyclic products [1, 2]. This has led to research to obtain the most reliable quantitative information on the effect of various internal and external factors (catalyst, solvent, temperature, high pressure) on the reaction rate, equilibrium and selectivity [2–4]. Huge amounts of accumulated experimental data have served as a basis for a number of theoretical models of cycloaddition reactions [3–6].

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The presence of an active diene or dienophile allows trapping of another reagent (dienophile/diene) in solution, polymers and biological objects. Among the dienophiles, the most active are tetracyanoethylene (**1**) and 4-phenyl-1,2,4-triazoline-3,5-dione (**2**), which are capable of fast reactions with a variety of dienes. Such reactions are often in the frame of “click-chemistry” [7]. There is an opportunity to use DAR to catch such carcinogenic impurities as anthracenes, benzantracenes, dibenzanthracenes and to neutralize them by transformation into less dangerous adducts. Some questions remained unanswered, such as why dienophile **2** with moderate electron affinity (E_A) may be more active in DAR with some dienes and vice versa with other dienes than tetracyanoethylene **1** with the highest π -electron affinity. The reactivity of “diene— π -donor, dienophile— π -acceptor” systems with C=C bonds in the DARs depends on the ionization potential (IP_D) of the dienes, electron affinity (E_A) of the dienophiles [$(IP_D - E_A)/\text{eV}$], energy balance of the breaking and forming of bonds ($\Delta H_{r-n}/\text{kJ}\cdot\text{mol}^{-1}$) and the 1–4 distance of reaction centers in 1,3-dienes ($R_{1-4}/\text{\AA}$), (Eq. 1, correlation coefficient, $r=0.972$; $n=93$) [3]:

$$\log_{10}k_2 = -28.81 + 316.3/(IP_D - E_A) - 69.9 \cdot R_{1-4}/(IP_D - E_A) - 0.054 \cdot \Delta H_{r-n} \quad (1)$$

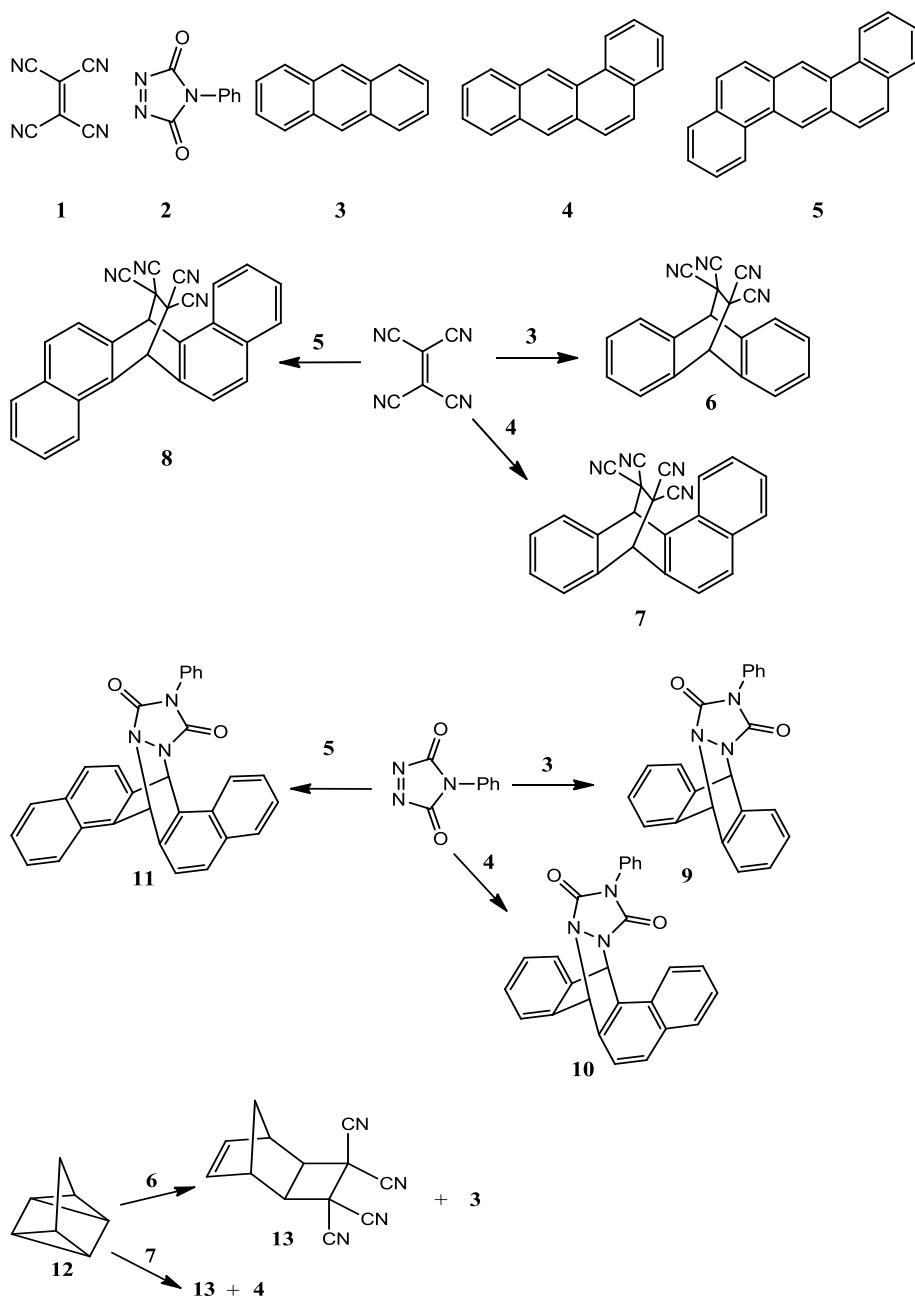
For this reason, *trans*-1,3-butadiene ($R_{1-4}=3.66 \text{ \AA}$) should be 8 orders of magnitude less active than *cis*-1,3-butadiene ($R_{1-4}=2.88 \text{ \AA}$). Hence it follows that the maximum of reactivity in the DAR should be observed for the planar *cis*-1,3-dienes with a minimum value of R_{1-4} . The energy balance of the reacting C=C bonds always affects the value of activation energy, but rarely governs the relative rate of the forward cyclization reaction [3]. Since the entropy values of the DARs are usually in the range $-(120\text{--}150) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ($298\cdot\Delta S^\ddagger \sim -40 \text{ kJ}\cdot\text{mol}^{-1}$), the reaction is thermodynamically favorable if the exothermicity of the DAR is higher than $-40 \text{ kJ}\cdot\text{mol}^{-1}$.

The relation (1) allows one to predict the activity of reagents with C=C bonds, since here the IP_D and E_A parameters are usually proportional to the charges at the reaction centers. The balance between the energies of rupture of C=C bonds in the reagents and formation of new C–C bonds in the products equals the enthalpy of the DAR. The changes in enthalpy values mainly reflect the difference in the conjugation energy of reacting C=C π -bonds [3]. The π -acceptor properties of **2** are rather moderate ($E_A \sim 1.0 \text{ eV}$) [8], and appreciably inferior to the dienophile of **1** ($E_A = 2.88 \text{ eV}$) [9]. On the other hand, the N=N bond disruption energy (418) is much less than that of the C=C bond (611 $\text{kJ}\cdot\text{mol}^{-1}$), which can be the main reason of a very high activity of **2**. In some cases the DARs can proceed rather fast, but with very low conversion, so it is important to consider both the kinetic and equilibrium parameters [3]. In this work the differences in the solvation enthalpies of reagents, transition state (TS) and adducts in the DAR of **1** and **2** with anthracene (**3**), 1,2-benzanthracene (**4**) and 1,2,5,6-dibenzanthracene (**5**) were determined on the basis of kinetic and thermochemical data (Scheme 1 of reactions).

2 Experimental Section

2.1 Chemicals Used

Tetracyanoethylene (**1**) and 4-phenyl-1,2,4-triazoline-3,5-dione (**2**) (Aldrich, 97%) were sublimated at $100 \text{ }^\circ\text{C}$ and 10 Pa before the measurements. White snow-like **1** had m.p. $200\text{--}201 \text{ }^\circ\text{C}$ (lit [10] $201 \text{ }^\circ\text{C}$) and red **2** had m.p. $165\text{--}170 \text{ }^\circ\text{C}$, with decomposition (lit [11] $165\text{--}170 \text{ }^\circ\text{C}$, decomp.). The purity of **2** was analyzed by the known absorption coefficient



Scheme 1 Scheme of reactions

in toluene ($\epsilon_{540 \text{ nm}} = 245$), 1,2-dichloroethane ($\epsilon_{540 \text{ nm}} = 178$), and in 1,4-dioxane ($\epsilon_{532 \text{ nm}} = 171 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) [12–14]. Anthracene (3), 1,2-benzanthracene (4) and 1,2,5,6-dibenzanthracene (5) (Aldrich, 99%) were used as purchased. All solvents were dried and purified by

known methods [15]. The UV spectra of solutions of reagents **1–5** in these solvents remained unchanged for at least one day.

2.2 Kinetic Measurements at Ambient Pressure

The temperature in the cell of the UV-spectrophotometer (Hitachi U-2900, Japan) was stable within ± 0.1 °C. The square-profiled sample cuvette ($1 \times 1 \times 4$ cm) made up of quartz was sealed with a ground glass stopper. The reaction rates with dienophile **2** were determined by following the absorption of dienophile **2** at 530–560 nm, and those of reactions with dienophile **1** were studied at 380–405 nm following the change in the absorption of the dienes **3–5**. The initial concentrations of dienophile **2** was 15–50 times lower than that of dienes **3–5**. The reaction rates with tetracyanoethylene in aromatic solvents were measured according to the change of the molecular complex's absorption at 450–550 nm.

The decomposition reactions $6 \rightarrow 1+3$ and $7 \rightarrow 1+4$ were carried out in the presence of quadricyclane (**12**), which rapidly ($k_2 = 104.4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) and irreversibly ($\Delta H_{r-n} = -236.6 \text{ kJ}\cdot\text{mol}^{-1}$) [16] binds dienophile **1**. The values of the rate constants were determined with errors not exceeding $\pm 3\%$, the enthalpies of activation $\pm 2 \text{ kJ}\cdot\text{mol}^{-1}$, and the entropies of activation $\pm 6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

2.3 Kinetic Measurements Under Elevated Pressure

The pressure effect on the rate of the reaction $2+4 \rightarrow 10$ was studied in toluene at 25 °C using the pressure multiplier (HP-500, Japan), a quartz cell with variable volume (PCI-500, Japan) and UV spectrophotometer (SCINCO S-3100, Korea). The observed activation volume ($\Delta V_{\text{exp}}^\ddagger$) of the reaction $2+4 \rightarrow 10$ ($C_{04} = C_{02} = 0.0103 \text{ mol}\cdot\text{L}^{-1}$) was calculated on the basis of the rate constants measured at ambient pressure and 1000 bar, applying the previously proposed [17] relationship (2).

$$(\partial \ln k / \partial P)_{T, P=1} = (1.15 \pm 0.03)^{-3} \times 10^{-3} \cdot \ln(k_{P=1000} / k_{P=1}) \quad (2)$$

$$\Delta V_{\text{exp}}^\ddagger = -R \cdot T \cdot (\partial \ln k / \partial P)_{T, P=1} \quad (3)$$

The corrected value of activation volume ($\Delta V_{\text{corr}}^\ddagger$) [18] of the reaction $2+4 \rightarrow 10$ was determined by Eqs. 3 and 4 taking into account the isothermal compressibility coefficient of toluene ($\beta_T = 9.19 \times 10^{-5} \text{ bar}^{-1}$) [19]:

$$\Delta V_{\text{corr}}^\ddagger = \Delta V_{\text{exp}}^\ddagger + \beta_T \cdot R \cdot T \quad (4)$$

2.4 Reaction Volumes in Solution

For reaction $2+4 \rightarrow 10$, the total volume of solution with reagents **2**, **4** and adduct **10** can be expressed by Eqs. 5–7:

$$V_{(t)} = V_s + (c_{0,2} - c_{10,t}) \cdot V_2 + (c_{0,4} - c_{10,t}) \cdot V_4 + c_{10,t} \cdot V_{10} \quad (5)$$

$$V_{(t)} = [V_s + (c_{0,2} \cdot V_2 + c_{0,4} \cdot V_4)] + c_{10,t} \cdot (V_{10} - V_2 - V_4) = V_{(t=0)} + c_{10,t} \cdot \Delta V_{r-n} \quad (6)$$

$$1/d_{(t)} = 1/d_{(t=0)} + c_{10,t} \cdot \Delta V_{r-n}/1000 \cdot d_{(t=0)} \quad (7)$$

Equation 7, derived from Eq. 6, is more convenient for determining the density 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 solvent volume; V_2 , V_4 , and V_{10} are the partial molar volumes of compounds **2**, **4**, and **10**; $c_{0,2}$, $c_{0,4}$, and $c_{10,t}$ are the initial molar concentrations of reagents **2** and **4**, and the current concentration of adduct **10**; ΔV_{r-n} is the reaction volume. The current concentration of adduct **10** was calculated from the kinetic data. Linear dependences $1/d_{(t)}$ versus c_{10} were observed for three measurements up to 95% conversion. A vibration densitometer (DSA 5000 M, Austria) was employed to measure the solution density ($\pm 2 \times 10^{-6} \text{ g}\cdot\text{cm}^{-3}$) at $25 \pm 0.002 \text{ }^\circ\text{C}$.

2.5 Calorimetric Experiment

The enthalpies of solution of the compounds were measured at $25 \text{ }^\circ\text{C}$ by the calorimetric method described previously [20]. The accuracy of the calorimeter was verified by comparing the heat of dissolution of dry potassium chloride in water at $25 \text{ }^\circ\text{C}$, $17.5 \pm 0.2 \text{ kJ}\cdot\text{mol}^{-1}$. The results are in a good agreement with the recommended data ($17.51 \pm 0.008 \text{ kJ}\cdot\text{mol}^{-1}$) [21]. The solid sample (30–50 mg) was added to a solvent (150 mL). Usually 3–4 consecutive dissolutions of each compound were carried out with a subsequent calibration of the calorimeter. The enthalpies of reactions were measured at $25 \text{ }^\circ\text{C}$ by addition of 20–40 mg of freshly sublimed **1** or **2** to the solution of the excess of diene, taking into account the heat of dissolving of **1** or **2**. The heat of slow reaction $\mathbf{2} + \mathbf{4} \rightarrow \mathbf{10}$ in 1,2-dichloroethane at $25 \text{ }^\circ\text{C}$ was measured using a ‘‘TAM III’’ precision solution calorimeter (USA), working in semi-adiabatic mode, using a 25 mL glass calorimetric vessel equipped with a gold stirrer, a Joule heater, and a thermistor. The calorimetric vessel was initially filled with 25 mL of a $0.0334 \text{ mol}\cdot\text{L}^{-1}$ solution of **4**. After about 1 h of thermostating and heater calibrations, a known volume of solution **2** ($0.191 \text{ mol}\cdot\text{L}^{-1}$) was added in portions of 60–80 μL from the electronically operated microsyringe.

2.6 Differences in Solvation Enthalpies

The transfer of solvation enthalpies of reagents ($\delta\Delta H_{\text{solv, reagent}}$), adducts ($\delta\Delta H_{\text{solv, add}}$) and transition state ($\delta\Delta H_{\text{solv, TS}}$) of the reactions $\mathbf{1} + \mathbf{3} \rightarrow \mathbf{6}$; $\mathbf{6} \rightarrow \mathbf{1} + \mathbf{3}$; $\mathbf{1} + \mathbf{4} \rightarrow \mathbf{7}$ and $\mathbf{2} + \mathbf{4} \rightarrow \mathbf{10}$ were calculated using acetonitrile as the reference solvent (Eqs. 8–10):

$$\delta\Delta H_{\text{solv, reagent}} = (\Delta H_{\text{dissolv, reagent}})_S - (\Delta H_{\text{dissolv, reagent}})_{\text{acetonitrile}} \quad (8)$$

$$\delta\Delta H_{\text{solv, add}} = (\Delta H_{\text{dissolv, add}})_S - (\Delta H_{\text{dissolv, add}})_{\text{acetonitrile}} \quad (9)$$

$$\delta\Delta H_{\text{solv, TS}} = \delta\Delta H_{\text{solv, reagent}} + \Delta H_S^\ddagger - \Delta H_{\text{acetonitrile}}^\ddagger \quad (10)$$

3 Results and Discussion

A set of data on the rate constants and the activation parameters of the forward ($\mathbf{1} + \mathbf{3} \rightarrow \mathbf{6}$) and backward ($\mathbf{6} \rightarrow \mathbf{1} + \mathbf{3}$) DARs in 14 solvents are collected in Table 1.

Table 1 The rate constants of forward (**1 + 3** → **6**) and backward (**6** → **1 + 3**) reactions, the equilibrium constant, enthalpy, entropy of activation and reaction, and the partial molar volume of tetracyanoethylene in 14 solvents at 25 °C

| N | Solvent/ $E_T(30)^a$ | k_f^b (L·mol ⁻¹ ·s ⁻¹) | ΔH_f^\ddagger (kJ·mol ⁻¹) | $-\Delta S_f^\ddagger$ (J·mol ⁻¹ ·K ⁻¹) | $k_r \times 10^6$ (s ⁻¹) | ΔH_r^\ddagger (kJ·mol ⁻¹) | ΔS_r^\ddagger (J·mol ⁻¹ ·K ⁻¹) | $K_{eq} \times 10^{-5}$ (L·mol ⁻¹) | $-\Delta H_{r-e}$ (kJ·mol ⁻¹) | $-\Delta S_{r-e}$ (J·mol ⁻¹ ·K ⁻¹) | V_1^\ddagger (cm ³ ·mol ⁻¹) |
|----|------------------------------------|---|---|--|--------------------------------------|---|---|--|---|---|--|
| 1 | 1,4-Dioxane/36.0 | 0.34 | 35.5 | 136 | 1.38 | 114 | 25 | 2.46 | 78.5 | 161 | 105.7 |
| 2 | Cyclohexanone/39.8 | 0.20 | 40.3 | 124 | 1.29 | 113 | 20 | 1.55 | 72.7 | 144 | 110.4 |
| 3 | Ethyl acetate/38.1 | 0.24 | 32.6 | 146 | 1.02 | 110 | 9 | 2.35 | 77.4 | 155 | 112.1 |
| 4 | Methyl acetate/38.8 | 0.36 | 31.9 | 146 | 1.43 | 112 | 18 | 2.52 | 80.1 | 164 | – |
| 5 | Acetonitrile/45.6 | 2.18 | 31.4 | 135 | 1.81 | 112 | 20 | 12.0 | 80.6 | 155 | 108.7 |
| 6 | 1,1,2,2-Tetrachloro-ethane/39.4 | 15.2 | 20.9 | 152 | 5.21 | 101 | -5 | 29.1 | 80.1 | 147 | – |
| 7 | 1,2-Dichloroethane/41.3 | 3.82 | 25.7 | 144 | 3.36 | 109 | 14 | 11.4 | 83.3 | 158 | 107.8 |
| 8 | Dichloromethane/40.7 | 4.28 | 26.4 | 140 | 4.54 | 100 | 13 | 9.43 | 73.6 | 127 | 107.5 |
| 9 | Trichloromethane/39.1 | 5.47 | 18.1 | 171 | 5.45 | 100 | -10 | 10.0 | 81.9 | 161 | 108.9 |
| 10 | Chlorobenzene/36.8 | 1.82 | 31.2 | 135 | 3.36 | 110 | 20 | 5.42 | 78.8 | 155 | 109.2 |
| 11 | Benzene/34.3 | 0.38 | 38.8 | 124 | 3.16 | 105 | 3 | 1.19 | 66.2 | 127 | 108.4 |
| 12 | Toluene/33.9 | 0.13 | 45.3 | 107 | 2.56 | 107 | 7 | 0.51 | 61.7 | 114 | 104.6 |
| 13 | <i>o</i> -Xylene/33.1 ^d | 0.06 | 50.4 | 100 | 2 ^e | 106 ^e | 6 ^e | 0.3 | 56 ^e | 102 ^e | 102.1 |
| 14 | Mesitylene/32.9 | 0.01 | 53.0 | 105 | 2 ^e | 106 ^e | 1 ^e | 0.05 | 53 ^e | 105 ^e | 98.1 |

^aEmpirical parameters of solvent polarity from [15]

^bIn some solvents the data were obtained earlier [22, 23] and are in good agreement with the presented data

^cData from [24]

^dData $E_T(30)$ for *p*-xylene

^eEstimated data from the cross-correlations

The rate constants of the forward reaction have decreased by almost 1500 times from 1,1,2,2-tetrachloroethane to the nonpolar mesitylene. This is mainly determined by a change in the activation enthalpy. Reduced reaction rates are observed in the oxygen-containing *n*-donor solvents (entries 1–4) and in π -donor alkylbenzenes (entries 11–14). In chloroalkanes (entries 6–9, Table 1) the reaction rates are increased. Note, that the rate constants of the adduct's decay ($6 \rightarrow 1+3$) and the activation enthalpies in all these solvents differ insignificantly (Table 1). It can be presumed that the solvent influence on the enthalpies of the reagents and the transition state for the direct DAR $1+3 \rightarrow 6$ are significantly different, in contrast to the retro reaction $6 \rightarrow 1+3$. In order to carry out a quantitative analysis of the change in the TS enthalpy, the thermochemical data on the change in the dissolution enthalpies of the reagents and reaction products in addition to the kinetic data are needed. These data, as well as the enthalpies of the reaction in the studied solvents are collected in Table 2.

The reliability of the dissolution heats (ΔH_{dissol}) and reaction heats (ΔH_{r-n}) in the studied solvents (Table 2) can be checked using the Hess law by calculating the standard enthalpy of reaction $1+3 \rightarrow 6$ ($\Delta H_{r-n, \text{ (st.st.)}}$) (Eq. 11):

$$\Delta H_{r-n, \text{ (st.st.)}} = \Delta H_{r-n}(\text{S}) + \Delta H_{\text{dissol}(1+3)}(\text{S}) - \Delta H_{\text{dissol}6}(\text{S}) \quad (11)$$

The data were not obtained in aromatic solvents (entries 10–14) due to the very low solubility of adduct **6**. Very close values of $\Delta H_{r-n, \text{ (st.st.)}}$ ($-40.5 \pm 0.6 \text{ kJ}\cdot\text{mol}^{-1}$, entries 1–9, Table 2) confirm the reliability of the obtained parameters. The dissolution heat of the adduct **6** can be calculated from Eq. 11 when the values of $\Delta H_{r-n}(\text{S})$ and $\Delta H_{\text{dissol}(1+2)}(\text{S})$ are known. In the series of solvents (entries 6–10) the dissolution heat of **1** is close to its fusion heat, $24.9 \text{ kJ}\cdot\text{mol}^{-1}$ [25], and the reaction rates are increased in these solvents. The correlations between the change in the enthalpy of solvation of **1** (entries 10–14) and the enthalpy of formation of the π,π -complexes [26], the partial molar volumes of **1** [24], the charge transfer energy of the band of these π,π -complexes with the solvents, and the changes of the DAR rates [3, 6, 24] (all $r > 0.95$) are clearly manifested. Similar changes in the solvation enthalpy of the reagents ($\delta H_{\text{solv}(1+3)}$) and the adduct ($\delta H_{\text{solv}6}$) are observed in the solvents (entries 1–10, Table 2) with an angular coefficient (0.85) close to unity, $r = 0.98$, $n = 10$ (Fig. 1, line *a*). The strong specific interaction of **1** with benzene, toluene, *o*-xylene and mesitylene disappears upon transition to the adduct **6**.

The changes in the enthalpies of solvation of TS are calculated (Eqs. 12 and 13) for the forward ($\delta \Delta H_{\text{solv TS}(1)}$) and reverse ($\delta \Delta H_{\text{solv TS}(-1)}$) DARs (Table 2):

$$\delta \Delta H_{\text{solv TS}(1)} = \Delta H_{(1)}^{\ddagger}(\text{S}) - \Delta H_{(1)\text{acetonitrile}}^{\ddagger} + \delta \Delta H_{\text{solv}(1+3)} \quad (12)$$

$$\delta \Delta H_{\text{solv TS}(-1)} = \Delta H_{(-1)}^{\ddagger}(\text{S}) - \Delta H_{(-1)\text{acetonitrile}}^{\ddagger} + \delta \Delta H_{\text{solv}(6)} \quad (13)$$

In all solvents the changes in enthalpy of solvation of TS ($\delta \Delta H_{\text{solv TS}}$) for direct $1+3 \rightarrow 6$ and reverse $6 \rightarrow 1+3$ reactions coincide within the total error of its determination ($\pm 6 \text{ kJ}\cdot\text{mol}^{-1}$). Attention should be paid at the increased stabilization of the TS in H-donor solvents, 1,1,2,2-tetrachloroethane and trichloromethane (Table 2). The enthalpy of the TS is insensitive to the π -donor properties of the solvents, in contrast to that of the reagents (entries 10–14, Table 2). Very close kinetic parameters for retro-DAR in the all studied media correspond to a loss of the π -acceptor properties on the way from tetracyanoethylene (**1**) to the TS and adduct **6** of reaction $1+3 \rightarrow 6$.

Table 2 The enthalpies of dissolution of reagents **1**, **3** and adduct **6**, the enthalpy of reaction **1** + **3** → **6**, the difference of activation enthalpies, the solvation transfer enthalpies of reagents (**1**, **3**), adduct **6** and transition state for the forward and backward reactions at 25 °C

| N | Solvent | ΔH_{dissol} (kJ·mol ⁻¹) | | | $-\Delta H_{\text{r-h}}^{\text{ts}}$ (kJ·mol ⁻¹) | $-(\Delta H_{\text{f}}^{\ddagger} - \Delta H_{\text{r}}^{\ddagger})^{\text{b}}$ (kJ·mol ⁻¹) | $-\Delta H_{\text{r-h}}^{\text{st}}$ ^c (kJ·mol ⁻¹) | $\delta\Delta H_{\text{sovl}}^{\text{d}}$ (kJ·mol ⁻¹) | | | |
|----|---------------------------|--|------|-------------------|---|--|--|---|----------------|-----------------|------------------|
| | | (1) | (3) | (6) | | | | (1, 3) | (6) | TS ₁ | TS ₋₁ |
| 1 | 1,4-Dioxane | 4.3 | 22.7 | -7.5 | 75.3 | 78.5 | 40.8 | -16.2 | -11.9 | -12.2 | -9.9 |
| 2 | Cyclohexanone | 7.6 | 20.6 | -4.4 | 73.7 | 72.7 | 41.1 | -14.9 | -8.8 | -6.1 | -7.7 |
| 3 | Ethyl acetate | 9.2 | 25.1 | -2.7 | 77.0 | 77.4 | 39.9 | -8.9 | -7.1 | -7.7 | -9.1 |
| 4 | Methyl acetate | 10.6 | 25.1 | -2.4 | 78.0 | 80.1 | 40.0 | -7.6 | -6.7 | -7.1 | -6.7 |
| 5 | Acetonitrile | 15.2 | 28.0 | 4.4 | 78.7 | 80.5 | 39.9 | (0) | (0) | (0) | (0) |
| 6 | 1,1,2,2-Tetrachloroethane | 19.3 | 18.6 | 3.5 | 74.2 | 80.2 | 39.8 | -5.3 | -0.9 | -15.9 | -11.9 |
| 7 | 1,2-Dichloroethane | 21.4 | 24.9 | 8.6 | 77.6 | 83.3 | 39.9 | 3.1 | 4.2 | -2.6 | 1.2 |
| 8 | Dichloromethane | 23.5 | 25.1 | 11.6 | 77.6 | 73.5 | 40.5 | 5.3 | 7.2 | 0.3 | -4.8 |
| 9 | Trichloromethane | 24.5 | 20.8 | 11.5 | 76.0 | 81.9 | 42.3 | 2.1 | 7.2 | -11.3 | -4.9 |
| 10 | Chlorobenzene | 22.2 | 24.6 | 8.5 ^e | - | 78.9 | 40.5 ^f | 3.6 | 4.1 | 3.3 | 2.1 |
| 11 | Benzene | 14.9 | 24.7 | 13.9 ^g | 68.4 | 66.3 | 40.5 ^f | -3.6 | 9.5 | 3.7 | 2.5 |
| 12 | Toluene | 9.8 | 24.8 | 13.4 ^g | - | 61.7 | 40.5 ^f | -8.7 | 8.9 | 5.2 | 4.1 |
| 13 | <i>o</i> -Xylene | 1.4 | 24.0 | 13.7 ^g | - | - | 40.5 ^f | -17.9 | 9 ^g | 1.2 | - |
| 14 | Mesitylene | -2.2 | 24.0 | 13.7 ^g | - | - | 40.5 ^f | -21.4 | 9 ^g | 0.6 | - |

^aThe values of calorimetric measurements in solution

^bThe enthalpy activation differences of forward and backward reactions

^cCalculated by Eq. 11

^dCalculated by Eqs. 8–10

^eEstimated by Eq. 11

^fThe mean value (Eq. 11, entries 1–9)

^gEstimated data from the cross-correlations

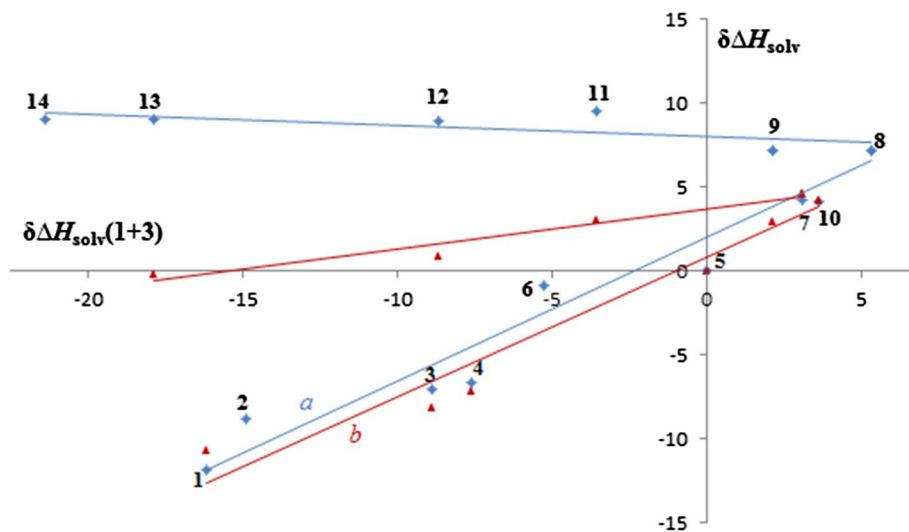


Fig. 1 Comparison of the changes in solvation enthalpy of tetracyanoethylene and anthracene ($\delta\Delta H_{\text{solv}}(1+3)$) relative to that of adduct ($\delta\Delta H_{\text{solv } 6}$), (filled blue diamond, $\delta\Delta H_{\text{solv } 6} = 0.85 \cdot \delta\Delta H_{\text{solv } (1+3)} + 2.05$; $r = 0.9643$, entries 1–8), and ($\delta\Delta H_{\text{solv } (1+3)}$) relative to that of 4-phenyl-1,2,4-triazoline-3,5-dione and anthracene ($\delta\Delta H_{\text{solv } (2+3)}$), (filled red triangle, $\delta\Delta H_{\text{solv } (2+3)} = 0.83 \cdot \delta\Delta H_{\text{solv } (1+3)} + 0.82$; $R = 0.9769$, entries 1–10). The solvent numerical designators are the same as in Table 2 (Color figure online)

Similar measurements were also performed for the DAR of anthracene (**3**) with 4-phenyl-1,2,4-triazoline-3,5-dione (**2**) (Table 3).

The changes in the enthalpy of solvation of reagents **2** and **3** (entries 1–9, Table 3) are proportional to those of reagents **1** and **3** (Fig. 1, line *b*, slope = 0.88, $r = 0.98$). The moderate π -acceptor properties of **2** are clearly manifested through a weak change in its enthalpy of dissolution and slight changes of the rate of reaction **2** + **3** \rightarrow **9** in aromatic solvents (entries 10–14, Table 3). The increased stabilization of the TS in reaction **2** + **3** \rightarrow **9** is observed again in H-donor solvents (entries 7, 9, Table 3). In all solvents the reaction **2** + **3** \rightarrow **9** is more exothermic than reaction **1** + **3** \rightarrow **6** by about 20 kJ·mol⁻¹. The decay rate of adduct **9** has not been studied, since the half-life of adduct **9** decomposition at 25 °C is estimated to be more than 2 years. Data for the reaction of tetracyanoethylene with 1,2-benzanthracene (**1** + **4** \rightarrow **7**) are collected in Table 4.

It can be expected that the difference in enthalpy of reaction **2** + **3** \rightarrow **9** and **1** + **3** \rightarrow **6** (about 20 kJ·mol⁻¹, Table 3) is due to the difference in the balance of the bond energies of dienophiles **1** and **2** in the DAR with any diene. An increase in the conjugation energy of diene **4** compared with **3** [27] leads to the fact that the equilibrium constant of reaction **1** + **4** \rightarrow **7** (Table 4) is almost 3 orders of magnitude lower than that for the reaction **1** + **3** \rightarrow **6**.

The reaction rate of tetracyanoethylene with dibenzanthracene **1** + **5** \rightarrow **8** was not determined because of the very low stability of adduct **8** in solution. It is interesting to note that the rates of reactions **2** + **4** \rightarrow **10** and **1** + **4** \rightarrow **7** in acetonitrile are very close. However, due to the same reasons the reaction **2** + **4** \rightarrow **10** in π -donor toluene proceeds already 30 times faster than **1** + **4** \rightarrow **7**. The rate of reaction **2** + **5** \rightarrow **11** (5.30×10^{-3} L·mol⁻¹·s⁻¹, Table 4) is significantly less than those of reactions **2** + **4** \rightarrow **10** (0.165) and **2** + **3** \rightarrow **9** (1.55 L·mol⁻¹·s⁻¹) in accordance with the change in conjugation energy of these dienes [27].

Table 3 Comparison of the rate constants, the enthalpies of activation, the enthalpies of dissolution of reagents (1–3) and adduct (6), the solvation transfer enthalpies of reagents and transition states, and the enthalpies of reactions in solution at 25 °C

| N | Solvent | k_2 (L·mol ⁻¹ ·s ⁻¹) | ΔH^\ddagger (kJ·mol ⁻¹) | | | | | ΔH_{dissol} (kJ·mol ⁻¹) | | | | | $\delta\Delta H_{\text{sol}}^{\text{Solv}}$ (kJ·mol ⁻¹) | | | | | $-\Delta H_{r-p}$ (kJ·mol ⁻¹) |
|----|---------------------------|---|---|-------|-------|-------|------|--|-------------------|-------|-------|-------|---|-------|-------|-------|-------|---|
| | | | 1+3→6 | 2+3→9 | 1+3→6 | 2+3→9 | 1 | 2 | 3 | 6 | (1,3) | (2,3) | 1+3→6 | 2+3→9 | 1+3→6 | 2+3→9 | 1+3→6 | |
| 1 | 1,4-Dioxane | 0.34 | 0.094 | 35.5 | 43.9 | 4.3 | 8.8 | 22.7 | -7.5 | -16.2 | -10.7 | -12.2 | -5.3 | 75.3 | 89.6 | | | |
| 2 | Cyclohexanone | 0.20 | - | 40.3 | - | 7.6 | - | 20.6 | -4.4 | -14.9 | - | -6.1 | - | 73.7 | - | | | |
| 3 | Ethyl acetate | 0.24 | 0.057 | 32.6 | 48.5 | 9.2 | 9.0 | 25.1 | -2.7 | -8.9 | -8.1 | -7.7 | 1.9 | 77.0 | 91.4 | | | |
| 4 | Methyl acetate | 0.36 | 0.070 | 31.9 | 46.4 | 10.6 | 9.9 | 25.1 | -2.4 | -7.6 | -7.2 | -7.1 | 0.7 | 78.0 | - | | | |
| 5 | Acetonitrile | 2.18 | 0.32 | 31.4 | 38.5 | 15.2 | 14.2 | 28.0 | 4.4 | (0) | (0) | (0) | (0) | 78.7 | 98.6 | | | |
| 6 | 1,1,2,2-Tetrachloroethane | 15.2 | - | 20.9 | - | 19.3 | - | 18.6 | 3.5 | -5.3 | - | -15.9 | - | 74.2 | - | | | |
| 7 | 1,2-Dichloroethane | 3.82 | 1.55 | 25.7 | 28.0 | 21.4 | 21.9 | 24.9 | 8.6 | 3.1 | 4.6 | -2.6 | -5.9 | 77.6 | 104.6 | | | |
| 8 | Dichloromethane | 4.28 | - | 26.4 | - | 23.5 | - | 25.1 | 11.6 | 5.3 | - | 0.3 | - | 77.6 | - | | | |
| 9 | Trichloromethane | 5.47 | 5.09 | 18.1 | 23.4 | 24.5 | 24.4 | 20.8 | 11.5 | 2.1 | 3.0 | -11.3 | -12.1 | 76.0 | 112.1 | | | |
| 10 | Chlorobenzene | 1.82 | 1.01 | 31.2 | 31.8 | 22.2 | 21.8 | 24.6 | 8.5 ^a | 3.6 | 4.2 | 3.3 | -2.5 | 78.9 | 99.6 | | | |
| 11 | Benzene | 0.38 | 0.52 | 38.8 | 35.1 | 14.9 | 20.6 | 24.7 | 13.9 ^a | -3.6 | 3.1 | 3.7 | -0.3 | 68.4 | 96.7 | | | |
| 12 | Toluene | 0.13 | 0.33 | 45.3 | 43.1 | 9.8 | 18.3 | 24.8 | 13.4 ^a | -8.7 | 0.9 | 5.2 | 5.5 | 61.7 | 95.0 | | | |
| 13 | <i>o</i> -Xylene | 0.061 | 0.21 | 50.4 | 46.0 | 1.4 | 18.0 | 24.0 | 13.7 ^b | -17.9 | -0.2 | 1.2 | 7.3 | - | 95.1 | | | |
| 14 | Mesitylene | 0.010 | - | 53.0 | - | -2.2 | - | 24.0 | 13.7 ^b | -21.4 | - | 0.2 | - | - | - | | | |

^aEstimated by Eq. 11

^bEstimated data from the cross-correlations

Table 4 The rate constants, enthalpies and entropies of activation, the enthalpies of dissolution, the solvation transfer enthalpies of reagents and transition states, and the enthalpies of reaction in solution of the DARs 1,2-benzanthracene with tetracyanoethylene (**1+4**→**7**) and 1,2-benzanthracene with 4-phenyl-1,2,4-triazoline-3,5-dione (**2+4**→**10**) at 25 °C

| Solvent | k_2 (L·mol ⁻¹ ·s ⁻¹) | | ΔH^\ddagger (kJ·mol ⁻¹) | $-\Delta S^\ddagger$ (J·mol ⁻¹ ·K ⁻¹) | ΔH_{dissol} (kJ·mol ⁻¹) | | $\delta\Delta H_{\text{sol, reagent}}$ (kJ·mol ⁻¹) | $\delta\Delta H_{\text{sol, TS}}$ (kJ·mol ⁻¹) | $-\Delta H_{\text{reagent}}$ (kJ·mol ⁻¹) | |
|------------------------|---|---|---|--|--|------|--|---|--|-----------------|
| | 15 °C | 25 °C | | | 4 | 1 | | | | 2 |
| 1+4 → 7 | | | | | | | | | | |
| Acetonitrile | 1.83×10 ⁻² | 2.97×10 ⁻² 3.61×10 ^{-5a} | 5.26×10 ⁻² | 36.4 | 152 | 21.1 | 15.2 | 14.2 | (0) | – |
| 1,2-Dichloroethane | 1.70×10 ⁻² | 3.18×10 ⁻² 1.24×10 ^{-5a} | 5.40×10 ⁻² | 40.2 | 138 9 ^a | 18.6 | 21.4 | 21.9 | 3.7 | 7.5 |
| Toluene | 2.80×10 ^{-3b} | 5.01×10 ^{-5a} 7.05×10 ⁻⁴ 4.41×10 ^{-5a} | 1.73×10 ^{-4a} | 94.8 ^a | 131 | 18.0 | 9.8 | 18.3 | -8.5 | 6.5 |
| 2+4 → 10 | | | | | | | | | | |
| Acetonitrile | 1.61×10 ⁻² | 3.20×10 ⁻² | 5.80×10 ⁻² | 44.9 | 123 | 21.1 | 15.2 | 14.2 | (0) | – |
| 1,2-Dichloroethane | 5.86×10 ⁻² | 1.05×10 ⁻¹ | 1.65×10 ⁻¹ 5.30×10 ^{-3d} | 35.8 | 144 | 18.6 | 21.4 | 21.9 | 5.2 | 73 ^c |
| Toluene | 1.12×10 ⁻² | 2.14×10 ⁻² | 3.98×10 ⁻² | 44.3 | 128 | 18.0 | 9.8 | 18.3 | 1.0 | 0.4 |

^aData of the reverse reaction **7**→**1+4**

^bData of forward reaction **1+4**→**7** at 45 °C

^cThe enthalpies activation difference of forward **1+4**→**7** and reverse **7**→**1+4** reactions

^dData of the reaction **2+5**→**11** at 35 °C

^eData of calorimetric measurements of reaction **2+4**→**10**

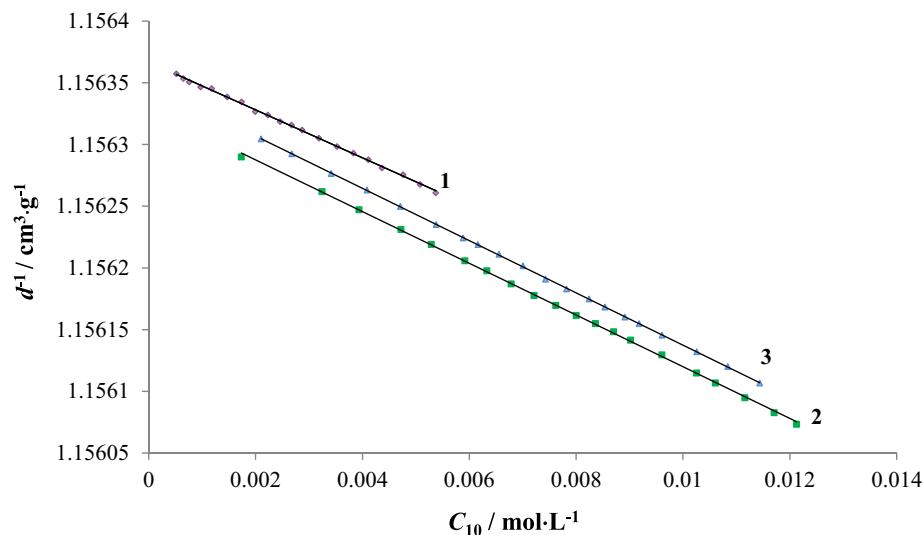


Fig. 2 The ratio between the specific volume of the solution ($d^{-1}/\text{cm}^3\cdot\text{g}^{-1}$) and the concentration of the adduct ($C_{10}/\text{mol}\cdot\text{L}^{-1}$) in the reaction $2+4\rightarrow 10$. **1** $d^{-1} = -(0.019443 \pm 0.000155) \cdot C_{10} + (1.158067 \pm 0.000005)$; $\Delta V_{r-n} = -16.8 \text{ cm}^3\cdot\text{mol}^{-1}$; $C_2 = C_4 = 5.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$; $r = 0.9995$. Curve **1** is shifted down by $0.0017 \text{ cm}^3\cdot\text{g}^{-1}$. **2** $d^{-1} = -(0.021016 \pm 0.000069) \cdot C_{10} + (1.156329 \pm 0.000006)$; $\Delta V_{r-n} = -18.2 \text{ cm}^3\cdot\text{mol}^{-1}$; $C_2 = 1.005 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $C_4 = 1.002 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$; $r = 0.9998$. **3** $d^{-1} = -(0.021187 \pm 0.000038) \cdot C_{10} + (1.156349 \pm 0.000003)$; $\Delta V_{r-n} = 18.3 \text{ cm}^3\cdot\text{mol}^{-1}$; $C_2 = 1.005 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $C_4 = 1.004 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$; $r = 0.9999$

The pressure effect on the rate of reaction $1+3\rightarrow 6$ has been described previously [3, 16, 24]. The rate of reaction $2+4\rightarrow 10$ was studied at ambient pressure [$k_2 = (2.04 \pm 0.02) \times 10^{-2}$] and at 1000 bar [$k_2 = (5.61 \pm 0.07) \times 10^{-2} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$] in toluene at 25 °C. The value of $\Delta V_{\text{exp}}^\ddagger$ is $-28.8 \pm 0.8 \text{ cm}^3\cdot\text{mol}^{-1}$ (Eqs. 2 and 3) and the corrected value (Eq. 4) of $\Delta V_{\text{corr}}^\ddagger$ is $-26.5 \pm 1.0 \text{ cm}^3\cdot\text{mol}^{-1}$. The value of the reaction volume (ΔV_{r-n}) has been determined from three measurements (Fig. 2).

The mean value of ΔV_{r-n} is $-17.8 \pm 0.6 \text{ cm}^3\cdot\text{mol}^{-1}$. Note that the volume of the TS in the reaction $2+4\rightarrow 10$ is $8.7 \text{ cm}^3\cdot\text{mol}^{-1}$ is more compact than the volume of adduct **10**. The ‘anomalies’, when $\Delta V_{\text{corr}}^\ddagger/V_{r-n} > 1$, for the isopolar DARs are due to the difficulties for the solvent molecules to approach the branched structures of the adducts [28].

4 Conclusions

The data obtained make it possible to explain the reasons for the sharp difference in the reactivity of tetracyanoethylene (**1**) and 4-phenyl-1,2,4-triazoline-3,5-dione (**2**) in the DARs with different dienes in different solvents. For the reaction of pronounced π -donor diene such as anthracene (**3**) ($IP_D = 7.40 \text{ eV}$) with a strong π -acceptor **1** ($E_A = 2.88 \text{ eV}$), the contribution of intermolecular stabilization energy is the determining parameter of the increased reaction rate with **1** compared with **2** (Table 3). There is a clear inversion of the reactivity for reagents **1** and **2** in the DARs with the less active dienes. The dienophile **2** is a moderate π -acceptor ($E_A \sim 1.0 \text{ eV}$), but disruption of N=N bonds is easier compared to the C=C bond in dienophile **1**. Tetracyanoethylene sharply loses its activity in aromatic

solvents due to complex formation with a solvent. The data obtained on the solvation enthalpy transfer of the reagents, products, and transition state clearly show that the acceptor properties of dienophile **1** disappear upon passage to TS and adduct. From obtained data (Tables 1–4) we can propose that an increased solvent influence on the reaction rate should be expected for all types of reactions involving tetracyanoethylene. The high rates for reactions involving very active dienophiles **1** and, especially, **2** can be useful to catch such carcinogenic impurities as **3–5** and neutralize them by transformation into less dangerous adducts.

Acknowledgements We are grateful to Dr. Igor Sedov for carrying out some calorimetric measurements. This work was supported by the Russian Foundation for Basic Research (Projects Nos. 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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