Why Can the Activation Volume of the Cycloadduct Decomposition in Isopolar Retro-Diels–Alder Reactions Be Negative?

VLADIMIR D. KISELEV

Butlerov Institute of Chemistry, Kazan State University, Kremlevskaja street, 18, Kazan, 420008, Russian Federation

Received 13 May 2009; revised 23 July 2009; accepted 7 September 2009

DOI 10.1002/kin.20462

ABSTRACT: Rate constants of the Diels–Alder cycloaddition reaction of anthracene with tetracyanoethylene, enthalpy of solution of reactants and adduct, enthalpy of the reaction in solution, enthalpy and entropy of activation of the forward and retro-Diels–Alder reactions were determined in 14 solvents. Temperature and pressure effects on the rate of the decomposition of the adduct formed from 9-chloroanthracene and tetracyanoethylene were studied. Since the electrostriction effect can be excluded from the consideration of the isopolar Diels–Alder reaction, negative values of the activation volume in the retro-Diels–Alder reactions can be caused by the different possibilities of penetration of the solvent molecules to large steric branched structures of the transition states and adducts. © 2009 Wiley Periodicals, Inc. Int J Chem Kinet 42: 117–125, 2010

INTRODUCTION

The main principles of direct Diels–Alder reactions (DARs) have been widely discussed [1,2] as compared with those of the corresponding retro process [3,4]. The intermolecular stabilization energy due to the orbital interaction between the π-donor diene and the π-acceptor dienophile can be very important for their reactivity [5].

There are many data on the pressure influence on the rate constants of forward DARs with a normal volume ratio of $\Delta V^{\neq}/\Delta V < 1$, where the activation volumes have less negative values than the reaction volumes [6–9]. This volume ratio is expected due to only partial new C—C bond formations in the transition state in contrast to the adduct. However, for about half of all experimental data found for the pressure effect on the rate of forward DARs another ratio, i.e., $\Delta V^{\neq}/\Delta V > 1$, was observed [6–9]. This means that in the last case the molar volume of the transition states (TS) should be more compact and smaller than that of the cycloadducts, and negative values of the volume of activation of retro DARs should be expected.

Correspondence to: Vladimir D. Kiselev; e-mail: vladimir.kiselev@ksu.ru.

Contract grant sponsor: Foundation for Basic Research.
Contract grant number: 08-03-00219.
Contract grant sponsor: U.S. Civilian Research and Development Foundation (CRDF), and the Ministry of Science and Education of the Russian Federation (Joint Program “Fundamental Research and High Education”).
Contract grant number: REC-007.

Considering DARs as an isopolar process [1,2,9], it is difficult to explain why the transition state with a partial C—C bonding should be more compact than that of the cycloadduct [10–16].

There are only a few direct measurements of the pressure influence on the rate of adduct decomposition, usually performed at elevated temperatures [10–13]. Eckert et al. have assumed that this abnormal ratio ($\Delta V_1^{\neq}/\Delta V_1 > 1$), observed mainly for the DARs with dipolar maleic anhydride or maleimide moieties, is most probably caused by the polarity effect [14,15]. Much attention has also been paid to "secondary attractive interactions," which could bear an additional volume contraction in the transition state and as a result the volume ratio is $\Delta V_1^{\neq}/\Delta V_1 > 1$ [9,14]. Presently, it is well established [6–8,16] that the value of the volume change due to secondary attractive interactions should be only about 1–2 cm^3 mol^{-1} and cannot explain this result. Moreover, an abnormal volume ratio of $\Delta V_1^{\neq}/\Delta V_1 > 1$ was observed for the DARs with formation of exo-adducts, where secondary attractive interactions should be excluded from mechanistic considerations [10,16–18].

It is desirable to consider the additional versions of generation of abnormal volume ratio, $\Delta V_1^{\neq}/\Delta V_1 > 1$.

In this work, rate constants of the Diels–Alder reaction of tetracyanoethylene (**1**) with anthracene (**2**), enthalpy of solution of reactants **1, 2**, and cycloadduct **3**, enthalpy of reaction (**1** + **2** → **3**), enthalpy and entropy of activation of the forward and retro-Diels–Alder reactions were determined in 14 solvents. Temperature and pressure effects on the rate of decomposition of the cycloadduct **5** formed from 9-chloroanthracene (**4**) and tetracyanoethylene (**1**) were also studied.

EXPERIMENTAL

Tetracyanoethylene (Merck, Germany) was sublimed in vacuum (110°C, 50 Pa). Anthracene and 9-chloroanthracene (Aldrich, Germany) were purified by column chromatography with neutral alumina oxide in the benzene-*n*-hexane (1:6) eluent.

Adducts **3** and **5** were obtained from equimolar benzene solutions of reagents **1, 2** and **1, 4**. They were crystallized with nearly quantitative yields. Adduct **6** was obtained by bubbling butadiene into the benzene solution of **1** up to its decoloration. Cyclopentadiene, obtained after cracking of dicyclopentadiene (150–160°C), was dried with molecular sieves (4 Å) and redistilled before use.

Rate measurements were performed following the change in the optical density of diene **2** or **4** at ν = 26,300 or 25,420 cm^{-1}, respectively. Because of the appreciable overlap of diene **4** fluorescence, its total absorption ($D_{(\mathbf{4})}$) was calculated as a function of the diene molarity ($C_{(\mathbf{4})}$):

$$(D_{(\mathbf{4})}) = A \ln\left[(C_{(\mathbf{4})} + B)/B\right] \qquad (1)$$

The coefficients (A) and (B) of Eq. (1) for all solutions are given in Table I.

The rate constants (Table II) of the formation of adduct **3** were calculated from the following relationship:

$$k_1 t C_{(\mathbf{1})} = \ln\left[D_{0,(\mathbf{2})}/D_{\mathrm{t},(\mathbf{2})}\right] \qquad (2)$$

Nearly the same results have been reported previously [19] for reaction (**1** + **2** → **3**), but with some erroneous values of entropy of activation. The rate constants of the decomposition of cycloadduct **3** (Table II) or **5** (Table I) were calculated from Eq. (3):

$$k_{-1} t = \ln\{[D_\infty/\varepsilon]/[D_\infty/\varepsilon - D_\mathrm{t}/\varepsilon]\} \qquad (3)$$

The absorption coefficient (ε) of diene **2** was assumed to be constant and that of diene **4** was calculated from Eq. (1). It was shown that the coefficients (A) and (B) of Eq. (1) (Table I) were invariable in the temperature range up to 50°C and under the pressure up to 1 kbar.

The procedure of high-pressure kinetics was described previously [12]. The decomposition rate of adduct **5** was changed to insight 40% at the pressure range from 1 bar to 1 kbar; therefore, the values of the activation volume were calculated from the values of the reaction rate constants at 1 bar and 1 kbar (Table I).

The values of the rate constants have been determined with errors of ±3%, enthalpy of activation ±1 kJ mol^{-1}, and entropy of activation ±3 J mol^{-1}K^{-1} for the forward reaction (**1** + **2** → **3**) and with errors of ±5%, ±2 kJ mol^{-1} and ±7 J mol^{-1}K^{-1}, respectively, for the decomposition of the adducts **3** and **5** (Tables I and II).

All calorimetric measurements (Table III) were performed as described elsewhere [20] with an accuracy of ±(0.5–1.0) kJ mol^{-1} for the enthalpy of solution of reactants ($\Delta_{\mathrm{sol}}H$) and ±(1.5–2.0) kJ mol^{-1} for enthalpy of reaction in solution ($\Delta_{r-n}H$).

At initial time, the zero value of the absorption of the solution with adduct **3** at ν = 26,300 cm^{-1} was in agreement with the absence of diene **2** as impurity. In addition, the control measurements of the heat of

Table I Rate Constants (k_{-1}/s^{-1}) in the Given Ranges of Temperature (t/°C) and Pressure (p/bar), Enthalpy ($\Delta H^{\neq}$/kJ mol^{-1}), Entropy ($\Delta S^{\neq}$/J mol^{-1} K^{-1}), and Volume ($\Delta V^{\neq}$/ cm^3 mol^{-1}) of Activation of the Decomposition of Cycloadduct **5**, Measured in Seven Solvents

No	Solvent	$10^4 k_{-1}/(t/°C)$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$10^4\ k_{-1}\ (p/\text{bar})^a$	$\Delta V^{\neq b}$	A^c	$10^4 B^c$
1	Acetonitrile	3.26(20); 6.05(25); 10.8(30); 19.6(35)	87.9	−12	3.26(1); 4.52(1000)	-7.9 ± 1.0	1.29	5.28
2	1,2- Dichloroethane	2.48(15); 4.51(20); 8.72(25); 15.0(30); 28.2(35)	87.0	−11	4.51^d	-6.5 ± 0.5^d	1.56	2.79
3	Chlorobenzene	2.45(15); 5.38(20); 9.64(25); 17.4(30)	91.2	+2	5.38(1); 5.90(1000)	-2.2 ± 1.0	2.20	3.28
4	Benzene	2.67(15); 8.95(25); 15.8(30)	83.3	−12	2.67(1); –^{e}	–	1.20	1.70
5	Toluene	2.28(15); 4.14(20); 7.92(25); 13.7(30);24.5(35)	85.4	−18	4.14(1); 5.60(1000)	-7.2 ± 1.5	1.63	2.49
6	Ethyl acetate	0.927(20); 1.89(25); 6.82(35); 23.2(45)	97.5	+10	0.927(1); 0.87(1000)	$+1.5 \pm 1.0$	1.45	7.02
7	*n*-Butyl acetate	0.854(20); 1.86(25); 3.70(30); 7.11(35); 14.1(40); 22.8(45)	100.4	+20	0.854(1); 0.75(1000)	$+3.0 \pm 1.0$	1.33	5.29

[a] Mean value at 20°C from triple measurements at 1 and 1000 bar.
[b] From Eq. (7) at 20°C.
[c] Coefficients of Eq. (1).
[d] From [12].
[e] Benzene solidifies at 550 bar and 20°C [9].

solution of adduct **3** were performed in the calorimetric cell without and in the presence of tetracyanoethylene (**1**) to exclude the possible decomposition of adduct **3** during the dissolution.

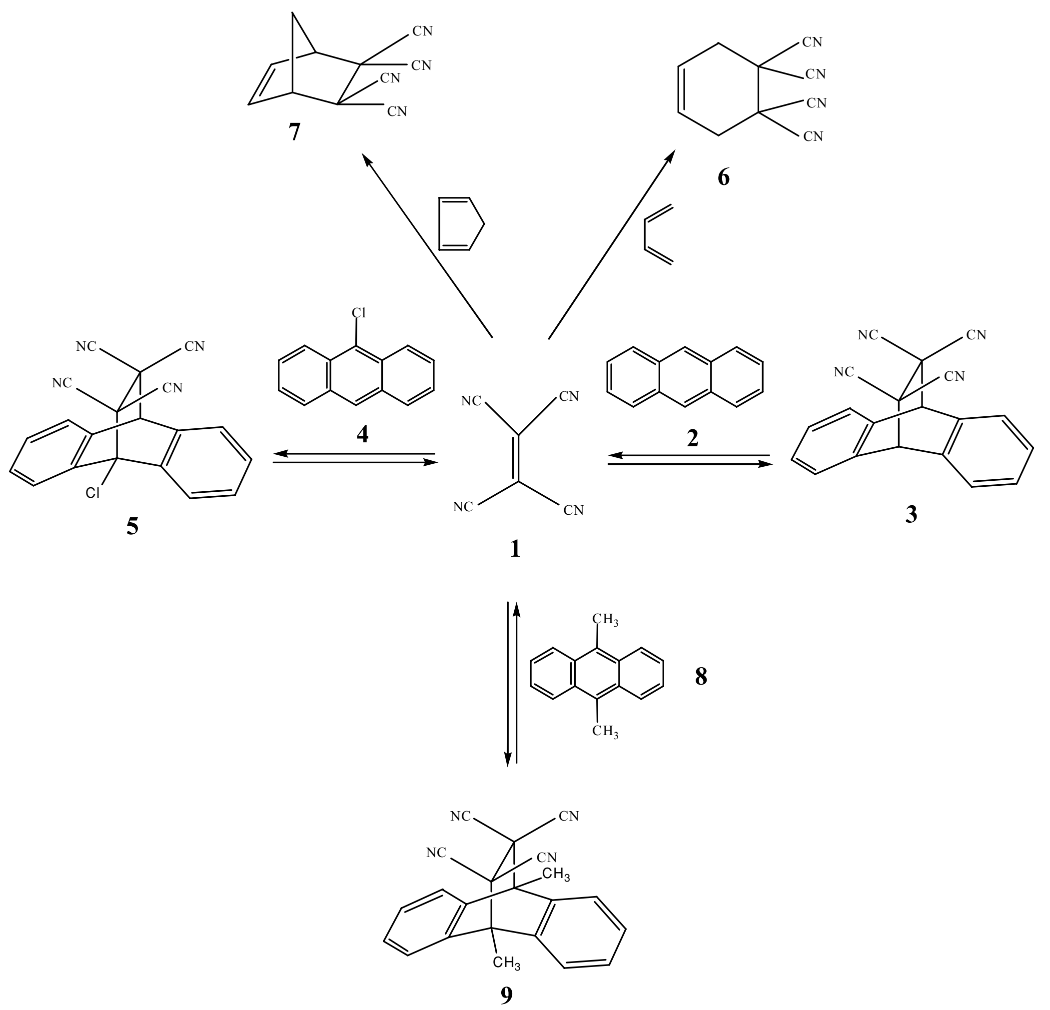
RESULTS AND DISCUSSION

Reactants and adducts should be convenient for monitoring of the reaction rates in both forward and backward directions. Reaction rate and enthalpy of activation of the retro-DARs studied are both very sensitive to the value of the reaction enthalpy. The reaction rate for $\mathbf{1} + \mathbf{2} \rightarrow \mathbf{3}$ is convenient for kinetic and calorimetric measurements at room temperature in the forward direction. Because of the large value of the equilibrium constant, a complete decomposition of the cycloadduct **3** can be realized in the case of diene **2** or dienophile **1** capture [12]. It was found that cyclopentadiene in solutions of cycloadduct **3** forms fast the stable cycloadduct **7** with intermediate **1**, and the effective rate was only limited by the rate of cycloadduct **3** decomposition. In Table II, the rate constants and activation parameters of the formation and decomposition of cycloadduct **3** are summarized.

There are linear regressions of solvent effects between the solvent-induced changes of the rate constants (ln k_1 vs. ln k_{-1}, $r = 0.94$), enthalpies ($\Delta H_1^{\neq}$ vs. $\Delta H_{-1}^{\neq}$, $r = 0.95$), and entropies ($\Delta S_1^{\neq}$ vs. $\Delta S_{-1}^{\neq}$, $r = 0.89$) of activation for the direct ($\mathbf{1} + \mathbf{2} \rightarrow \mathbf{3}$) and the retro ($\mathbf{3} \rightarrow \mathbf{1} + \mathbf{2}$) reaction (Table II) with relatively close values of ($\Delta H_1^{\neq} - \Delta H_{-1}^{\neq}$) and ($\Delta S_1^{\neq} - \Delta S_{-1}^{\neq}$), obtained in all studied solvents, except π-donor solvents (entries 11–14, Table II).

Calorimetric data on the heat of reaction ($\mathbf{1} + \mathbf{2} \rightarrow \mathbf{3}$) in solution ($\Delta_{r-n}H_{(\mathrm{Si})}$) and the heat of solution ($\Delta_{\mathrm{sol}}H_{(\mathrm{Si})}$) of reactants **1**, **2**, and cycloadduct **3** in the same solvents were also determined (Table III).

Unexpectedly, the dissolution of the crystalline cycloadduct **3** in some solvents (entries 1–4, Table III) was exothermic. This means stronger solvating interactions of the large, branched molecules of adduct **3** in solution compared with interactions appearing in the crystalline form. Exothermic heat of solution of crystal molecules of fullerenes, C_{60} and C_{70}, was also observed in some solvents. The solvent molecules are capable to fit more tightly to the surface of large "ball" molecules as compared with the intermolecular interactions in solid state [23,24]. Nearly, the same solvent effect on the enthalpy of solution of adduct **3** and **6** (Table III) was observed: $\Delta_{\mathrm{sol}}H_{(6)} = 17.5 + 0.37 \cdot \Delta_{\mathrm{sol}}H_{(3)}$; $r = 0.98$, $n = 10$).



The reliability of the measured calorimetric data can be proved by the constancy of the corresponding values of the heat of reaction (**1** + **2** → **3**) in the standard state ($\Delta_{r-n}H_{(\mathrm{st.st.})}$), that is in the solid state, 25°C, 1 atm:

$$\Delta_{r-n}H_{(\mathrm{st.st.})} = \Delta_{r-n}H_{(\mathrm{Si})} + \Delta_{\mathrm{sol}}H_{(1),(\mathrm{Si})} + \Delta_{\mathrm{sol}}H_{(2),(\mathrm{Si})} - \Delta_{\mathrm{sol}}H_{(3),(\mathrm{Si})} \qquad (4)$$

A close value of -40.6 ± 0.7 kJ mol^{-1} was obtained from these data (entries 1–9, Table III). For aromatic solvents with very poor solubility for cycloadduct **3**, the values $\Delta_{\mathrm{sol}}H_{(3)}$ can be calculated from Eq. (4). The relative changes of the enthalpy of solvation for the transition state were calculated for the forward ($\delta_{\mathrm{solv}}H_{(\mathrm{TS},1)}$) and the retro ($\delta_{\mathrm{solv}}H_{(\mathrm{TS},-1)}$) reactions corresponding to Eqs. (5) and (6):

$$\delta_{\mathrm{solv}}H_{(\mathrm{TS},1)} = \Delta_{\mathrm{sol}}H_{(\mathbf{1},\mathbf{2}),(\mathrm{Si})} - \Delta_{\mathrm{sol}}H_{(\mathbf{1},\mathbf{2}),(\mathrm{So})} + \Delta H^{\neq}_{(1),(\mathrm{Si})} - \Delta H^{\neq}_{(1),(\mathrm{So})} \qquad (5)$$

$$\delta_{\mathrm{solv}}H_{(\mathrm{TS},-1)} = \Delta_{\mathrm{sol}}H_{(\mathbf{3}),(\mathrm{Si})} - \Delta_{\mathrm{sol}}H_{(\mathbf{3}),(\mathrm{So})} + \Delta H^{\neq}_{(-1),(\mathrm{Si})} - \Delta H^{\neq}_{(-1),(\mathrm{So})} \qquad (6)$$

Owing to the same pathway for the forward and back DARs, the good linear correlations ($r = 0.97$, $n = 12$) between the independent values ($\delta_{\mathrm{sol}}H_{(\mathrm{TS},1)}$) and ($\delta_{\mathrm{sol}}H_{(\mathrm{TS},-1)}$) confirm the validity of these experimental data, included in Eqs (5) and (6).

It follows from obtained data (Tables II and III) that the changes of enthalpy of solvation of the TS ($\delta_{\mathrm{solv}}H_{(\mathrm{TS})}$) do not correlate ($r = 0.56$, $n = 10$) with the changes of enthalpy of solvation of cycloadduct **3**. These irregularities of the solvation of cycloadduct and TS can differently affect the partial molar volumes of the adduct ($V_{(\mathbf{3})}$) and the transition state (V_{TS}), and, consequently, the activation volume ($\Delta V^{\neq}_{-1}$) of the cycloadduct decomposition:

$$\partial \ln k_{-1}/\partial P = -(V_{\mathrm{TS}} - V_{(\mathbf{3})})/RT = -\Delta V^{\neq}_{-1}/RT \qquad (7)$$

Table II Rate Constants (k_1/l mol^{-1} s^{-1} and k_{-1}/s^{-1}) at 15, 25, 35, and 45°C; Enthalpy ($\Delta H^{\neq}$/kJ mol^{-1}) and Entropy ($\Delta S^{\neq}$/J mol^{-1} K^{-1}) of Activation for Forward (1) and Back (−1) Reactions of Anthracene with Tetracyanoethylene in 14 Solvents of Different Polarity

No	Solvent	k_1	$\Delta H_1^{\neq}$	$-\Delta S_1^{\neq}$	$10^6 k_{-1}$	$\Delta H_{-1}^{\neq}$	$\Delta S_{-1}^{\neq}$	$\Delta H_1^{\neq} - \Delta H_{-1}^{\neq}$	$\Delta S_1^{\neq} - \Delta S_{-1}^{\neq}$	$10^{-5} k_1/k_{-1}$[a]
1	1,4-Dioxane	0.202; 0.340; 0.521; 0.802	35.5	135	0.280; 1.38; 6.17; 25.0	114	25	−78.5	−160	2.46
2	Cyclohexanone	0.20[b]	40.3[b]	124[b]	0.258; 1.29; 5.54; 22.2	113	22	−72.7	−146	1.55
3	Ethyl acetate	0.151; 0.240; 0.366; 0.546	32.6	147	0.215; 1.02; 4.28; 16.5	110	10	−77.4	−157	2.35
4	Methyl acetate	0.228; 0.360; 0.544; 0.805	31.9	146	0.296; 1.43; 6.18; 24.5	112	19	−80.1	−165	2.52
5	Acetonitrile	1.41; 2.18; 3.30; 4.86	31.4	135	0.377; 1.82; 7.86; 31.1	112	21	−80.5	−156	12.0
6	1,1,2,2-Tetrachloroethane	11.3; 15.2; 19.9; 25.7	20.9	152	1.26; 5.21; 19.5; 67.5	101	−6	−80.2	−146	29.1
7	1,2-Dichloroethane	2.60; 3.82; 5.23; 7.18	25.7	147	0.780; 3.36; 13.1; 46.9	104	−0.5	−78.3	−146	11.4
8	Dichloromethane	2.92; 4.28; 5.98; -	26.4	144	1.04; 4.54; 18.0; -	105	5.3	−78.6	−149	9.43
9	Chloroform	4.23; 5.47; 6.91; 8.63	18.1	170	1.37; 5.45; 19.6; 65.2	98	−17	−79.9	−153	10.0
10	Chlorobenzene	1.17; 1.82; 2.72; 4.01	31.2	135	0.711; 3.36; 14.1; 53.3	110	20	−78.8	−155	5.42
11	Benzene	0.221; 0.380; 0.632; 1.02	38.8	123	0.720; 3.16; 12.4; 45.2	105	2	−66.2	−125	1.19
12	Toluene	0.064; 0.130; 0.220; 0.385	45.3	110	0.569; 2.56; 10.3; 38.6	107	7	−61.7	−117	0.51
13	*o*-Xylene	0.030; 0.061; 0.117; 0.215	50.4	99	–	–	–	–	–	(0.2)[c]
14	Mesitylene	0.0048; 0.0102; 0.0202; 0.0388	53.0	105	–	–	–	–	–	(0.03)[c]

[a] At 25°C.

[b] Data at 25°C from [19].

[c] Estimated data.

Table III Enthalpy of Solution ($\Delta_{\text{sol}}H$/kJ mol^{-1}) of Tetracyanoethylene (**1**), Anthracene (**2**), Their Adduct (**3**), Enthalpy of the Diels–Alder Reaction in Solution ($\Delta_{r-n}H_{(S)}$) and in the Standard State ($\Delta_{r-n}H_{(\text{st.st.})}$) as Well as the Relative Changes of Enthalpy of Solvation ($\delta_{\text{solv}}H$/kJ mol^{-1}) of Reagents (**1**, **2**), Cycloadduct (**3**), and Transition States (TS) for the Forward (1) and Back (−1) Reactions in 14 Solvents at 25°C

		$\Delta_{\text{sol}}H$				Δ_{r-n}	Δ_{r-n}	$\delta_{\text{solv}}H$			
No.	Solvent	**1**	**2**	**3**	**6**[a]	$H_{(S)}$	$H_{(\text{st.st.})}$	(**1** + **2**)	(**3**)	TS(1)	TS(-1)
1	1,4-Dioxane	4.3[b]	22.7[b]	−7.5	14.8	−75.3	−40.8	−16.2	−11.9	−12.2	−9.9
2	Cyclohexanone	7.6	20.6	−4.4	15.2	−73.7	−41.1	−14.9	−8.8	−6.1	−7.7
3	Ethyl acetate	9.2	25.1	−2.7	16.1	−77.0	−39.9	−8.9	−7.1	−7.7	−9.1
4	Methyl acetate	10.6	25.0	−2.4	16.7	−78.0	−40.0	−7.6	−6.7	−7.1	−6.7
5	Acetonitrile	15.2	28.0	4.4	20.2	−78.7	−39.9	(0)[c]	(0)[c]	(0)[c]	(0)[c]
6	1,1,2,2-Tetrachloroethane	19.3	18.6	3.5	–	−74.2	−39.8	−5.3	−0.9	−15.9	−11.9
7	1,2-Dichloroethane	21.4	24.9	8.6	21.6	−77.6	−39.9	3.1	4.2	−2.6	−3.8
8	Dichloromethane	23.4[d]	25.1[d]	11.6[d]	21.2	−77.7[d]	−40.5	5.3	7.2	0.3	0.2
9	Chloroform	24.5	20.8; 21.8[b]	11.5	21.1	−76.0	−42.3	2.1	7.2	−11.3	−6.9
10	Chlorobenzene	23.1; 22.2[b]	24.6[b]	8.5[e]	–	−78.8[f]	(−40.6)[g]	3.6	4.1	3.3	2.1
11	Benzene	14.9	24.7	13.9[e]	22.9	−66.3[f]	(−40.6)[g]	−3.6	9.5	3.7	2.5
12	Toluene	9.8	24.8	13.4[e]	22.5	−61.7[f]	(−40.6)[g]	−8.7	8.9	5.2	4.1
13	*o*-Xylene	1.4[b]	24.0	–	20.7	–	(−40.6)[g]	−17.9	–	1.2	–
14	Mesitylene	−2.2	24.0	–	–	–	(−40.6)[g]	−21.0	–	0.6	–

[a] Heat of solution of butadiene–tetracyanoethylene adduct.

[b] From [21].

[c] Acetonitrile was chosen as a blank.

[d] From [22].

[e] Calculated from Eq. (4).

[f] Calculated from the values ($\Delta H_1^{\neq} - \Delta H_{-1}^{\neq}$).

[g] Average value from the entries 1–9.

The rate of the decomposition of the adduct **5** was found to be faster and more convenient for the measurements under pressure, as compared with the adduct **3**, due to the large difference between the heat of reactions ($\Delta_{r-n}H_{(1+2)} = -77.6$ and $\Delta_{r-n}H_{(1+4)} = -66.0$ kJ mol^{-1} in 1,2-dichloroethane) [2]. All the results obtained for the decomposition of cycloadduct **5** are given in Table I.

A similar solvent influence ($r = 0.96$) on the rates of decomposition ($\ln k_{-1}$) of cycloadducts **3** and **5** was observed. The values of the activation volume were calculated (Eq. (7)) from pressure effects on the rate of adduct **5** decomposition. Negative values of the activation volume were obtained in acetonitrile, 1,2-dichloroethane, chlorobenzene, and toluene, and positive ones in ethyl acetate and *n*-butyl acetate solutions (Table I). Total difference of the values of the volume of activation ($\Delta V_{-1}^{\neq}$) is within of 10 cm^3 mol^{-1}. It should be noted that all the differences of the values of the volumes of activation ($\Delta V_1^{\neq}$) and volumes of DARs (ΔV) are within of 10 cm^3 mol^{-1} [6–9].

For reaction (**5** → **1** + **4**) (Table I), linear correlations between the volumes of activation and enthalpy of activation ($r = 0.97$) or entropy of activation ($r = 0.97$) were observed.

What can define abnormal ratio ($\Delta V_1^{\neq}/\Delta V_1 > 1$) in the forward DAR, generating less compact volume of adduct as compared with the TS?

Let us consider three possible reasons for the activation volume of the cycloadduct decomposition to be negative: (1) solvent electrostriction effects; (2) specific donor–acceptor interactions; and (3) mechanistic peculiarities of the solvent effect on the partial molar volume.

(1) Solvent electrostriction in a solvation shell of a charged particle can be large, resulting in values of the partial molar volume of some electrolytes to be very small and even negative [9,25,26]. The charge generation in the transition state should reduce its molar volume, and thereby electrostriction phenomena can explain all results: the ratio $\Delta V^{\neq}/\Delta V > 1$ for the forward DARs and the reason for negative values of the activation volume for retro-DARs [10,14–17]. But the very weak and irregular solvent influence on the rate of the direct [1,2,9,27] and especially retro-DARs (Tables I and II) allows one to consider the DAR as an isopolar process without an appreciable change of polarity on the way to the transition state.

(2) It was proved [5] that a molecular complex (MC) between tetracyanoethylene (**1**) and

9,10-dimethylanthracene (**8**) is preliminarily formed on the way to the cycloadduct **9**:

$$\mathbf{1} + \mathbf{8} \overset{K_{\mathrm{MC}}}{\rightleftharpoons} \mathrm{MC} \xrightarrow{k} \mathbf{9} \tag{8}$$

The negative value of the activation enthalpy has been calculated from the temperature dependence of an apparent rate constants ($k_{\mathrm{app}} = k \cdot K_{\mathrm{MC}}$), due to the larger value of enthalpy of the molecular complex formation ($|\Delta H_{\mathrm{MC}}|$) as compared to the activation energy ($\Delta H^{\neq}$). The same reaction scheme (8) can be assumed for the DARs of tetracyanoethylene with anthracene and 9-chloroanthracene. Similarly, the apparent activation volume of the forward DAR can be considered from the pressure dependence of the apparent rate constant ($k_{\mathrm{app}} = k \cdot K_{\mathrm{MC}}$) as

$$\Delta V^{\neq}_{\mathrm{app}} = \Delta V^{\neq} + \Delta V_{\mathrm{MC}} \tag{9}$$

The ΔV_{MC} values of the molecular complex formation of tetracyanoethylene (**1**) with 9-chloroanthracene (**4**), anthracene (**2**), and 9,10-dimethylanthracene (**8**) can be estimated from the dependence of the partial molar volume of **1** in aromatic π-donor solvents on the ionization potential of these solvents [28]:

$$V_{(\mathbf{1}),\mathrm{S}} = 22.3 + 9.3\mathrm{IP}_{\mathrm{S}};\ r = 0.99 \tag{10}$$

The partial molar volumes of tetracyanoethylene dissolved in π-donor solvents with ionization potentials of 7.74, 7.33, and 7.04 eV [2], as in dienes **4**, **2**, and **8**, can be estimated from Eq. (10) as 94.3, 91.4, and 87.8 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$, respectively. Acetonitrile, 1,2-dichloroethane, and dichloromethane (entries 5, 7, and 8 in Table III) can be considered as inert solvents, where the partial molar volumes of **1** are 110, 108, and 108 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$, respectively [28]. From these data, the calculated values ΔV_{MC} of molecular complexes (**1**–**4**), (**1**–**2**), and (**1**–**8**) are -14.4, -17.3, and -20.9 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$. The $\Delta V^{\neq}_{\mathrm{app}}$ value for the reaction ($\mathbf{1} + \mathbf{4} \rightarrow \mathbf{5}$) in 1,2-dichloroethane has been determined as -28.5 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ and the reaction volume $\Delta_{r-n}V$ as -22.0 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ [12]. Hence, the value of $\Delta V^{\neq}$ can be estimated by means of Eq. (9) as -14.1 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ (Fig. 1).

The same value of the molar volume of the transition state was calculated from the pressure effect on the rate constants of the forward and back reactions ($\mathbf{1} + \mathbf{4} \rightleftharpoons 5$) [12]. It was observed that the orientation of reactant molecules in the molecular complex is reconciled with the demand of the transition state structure [5]. Therefore, the additional enthalpy of activation for the case formation of MC on the way to TS should be less than in the process with a weak complex formation. The TS of the Diels–Alder reaction should be early, with the structure similar to structure of MC for the case with the very large energy of the intermolecular stabilization [1,2,5]. But even for the one of the strongest π-donor and π-acceptor pair (**8** and **1**), the values of the ΔV_{MC} and $\Delta_{r-n}V$ in 1,2-dichloroethane equal -20.9 and -22.0 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$, from which the positive value of $\Delta V^{\neq}_{(-1)}$ should be supposed here. Moreover, there are a lot of data with the ratio $\Delta V^{\neq}/\Delta V > 1$ for the forward [6–9] DARs and some direct measurements of the negative value of the $\Delta V^{\neq}_{(-1)}$ of the cycloadduct decompositions even for the systems with very weak donor–acceptor interactions [10,11,13].

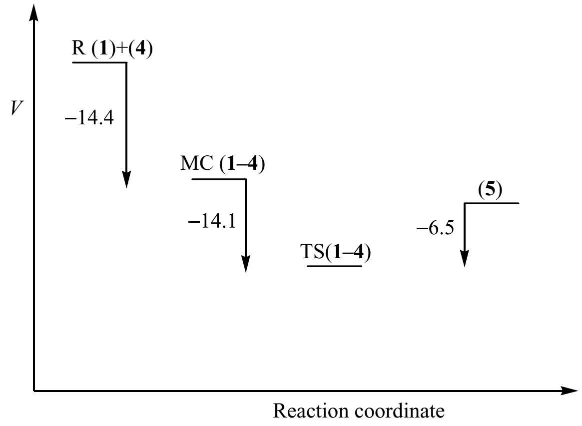


Figure 1 Volume changes ($\mathrm{cm}^3\ \mathrm{mol}^{-1}$) caused by the formation of the molecular complex (MC), the transition state (TS), and the adduct (**5**) from tetracyanoethylene (**1**) and 9-chloroanthracene (**4**), measured in 1,2-dichloroethane at 25°C.

Therefore, the intermediate formation of a molecular complex between the reactants cannot be either the reason for the negative value of activation volume of the cycloadduct decomposition.

(3) It is known that estimated van der Waals activation volumes, $\Delta V^{\neq}_{W(1)}$, should be negative for the direct DAR within -6 to -8 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$, and positive ($\Delta V^{\neq}_{\mathrm{W}(-1)} \sim +2$ $\mathrm{cm}^3\ \mathrm{mol}^{-1}$) for the retro reaction [10,16]. The reaction volumes of some DARs in the solid state were observed in the range -4 to -11 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ [29]. Significantly more negative values of the reaction volumes of the same reactions in solution (-20 to -35 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$) indicate that the volume parameters in solution are determined not only by the formation of new bonds in the cycloadduct. Additional volume contributions to $\Delta_{r-n}V$ (up to 75%) are created by decreasing of the volume of empty spaces in solution on the pathway from two reactants to one cyclic adduct [16,29]. However, from this consideration, the value of the volume of activation of the adduct decomposition always should be positive.

It can be suggested that in the common DAR van der Waals solute–solvent interactions, the different accessibility of the solvent to the steric branched structures can be the additional reason for the irregularity in the changes of the solvation energy and the partial molar volume. It is necessary to note that for different planar structures of dienes and dienophiles (except tetracyanoethylene), with the surfaces accessible for solvation, usually weak variety of the solvent effects on the values of partial molar volumes were observed [24,30]. On the other hand, the large differences of the partial molar volumes for the branched molecular structure of adducts were detected [6–8,31,32]. Thus, the partial molar volumes of the adduct formed from maleic anhydride with *trans*-1-methoxybutadiene are as follows: 144.6 in nitromethane; 137.0 in acetonitrile; 142.6 in 1.2-dichloroethane; 134.7 in 1-chlorobutane, and 139.7 cm^3 mol^{-1} in dimethyl carbonate [31]. Large solvent effects on the partial molar volumes of adduct **7** formed from tetracyanoethylene and cyclopentadiene were noted as well in benzene, 159.6; toluene, 158.3; *o*-xylene, 160.2; mesitylene, 159.4; chlorobenzene, 159.6; acetonitrile, 150.6; ethyl acetate, 150.3; cyclohexanone, 157.5; 1,4-dioxane, 151.6; dichloromethane, 153.7; and 1,2-dichloroethane, 154.7 cm^3 mol^{-1} [32]. These data illustrate the large differences in the partial molar volumes of cycloadducts, up to 10 cm^3 mol^{-1}, which are not related with the solvent polarity or donor–acceptor properties. There is no correlation of the partial molar volume (PMV) changes of adduct **7** in 11 solvents with the compressibility coefficients of these solvents (β_T, $r = -0.56$), or electrostriction parameters $\{\partial(1/\varepsilon)/\partial p$, $r = 0.41\}$. These differences in PMV can be attributed to the distinct accessibility of solvent molecules to the surface of adduct **7**. It should be noted that for DARs the ratio ($\Delta V^{\neq}/\Delta V > 1$) can be inverted ($\Delta V^{\neq}/\Delta V < 1$) with the solvent change [14,15].

Analysis of the literature data revealed the additional examples of irregular solvent effects on the partial molar volumes of steric hindered molecules [6–8,16,24,33]. The values of the partial molar volumes of branched structures of adamantane (136.9 and 142.7) and congressane (160.2 and 177.4 cm^3 mol^{-1}) in *n*-hexane and benzene differ sharply, depending on the solvent structure [24]. In spite of the total tendency of increasing of the molar volume under melting or dissolving, the value of the molar volume of crystalline fullerene C_{60} (429 cm^3 mol^{-1}) is larger than in all studied solvents [24]. Large changes of the partial molar volumes of C_{60} in solutions (from 350 to 400 cm^3 mol^{-1}) had been interpreted in terms of the "steric" effect on the solvation [24]. Larger volume of empty spaces between the "ball" molecules in solid C_{60} as compared with the solute–solvent in solution is the main reason for the reduction in the value of an apparent molar volume in solution [24] and an exothermic heat of C_{60} dissolution [23].

For the reason of all of these considerations, it can be proposed that unexpected negative values of the activation volume of the retro isopolar DARs and abnormal volume ratio $\Delta V^{\neq}/\Delta V > 1$ for forward isopolar DARs can be caused by the different capability of the solvent molecules to penetrate into the large steric branched structures of the transition states and adducts.

I am grateful to Dr. Helena Kashaeva and Alexander Bolotov for carrying out some measurements. I also appreciate fruitful comments from the reviewers, which helped in finalizing this paper.

BIBLIOGRAPHY

1. Sauer, J.; Sustmann, R. Angew Chem 1980, 92, 773–801.
2. Kiselev, V. D.; Konovalov, A. I. J Phys Org Chem 2009, 22, 466–483.
3. Herndon, W. C.; Hall, L. H. Tetrahedron Lett 1967, 8, 3095–3098.
4. Snyder, J. P.; Harp, D. N. J Am Chem Soc 1976, 98, 7821–7823.
5. Kiselev, V. D.; Miller, J. G. J Am Chem Soc 1975, 97, 4036–4039.
6. Asano, T.; le Noble, W. J. Chem Rev 1978, 78, 408–489.
7. van Eldik, R.; Asano, T.; le Noble, W. J. Chem Rev 1989, 89, 549–688.
8. Drljaca, A.; Hubbard, C. D.; van Eldik, R.; Asano, T.; Basilevsky, M. A.; le Noble, W. J. Chem Rev 1998, 98, 2167–2289.
9. Isaacs N. S. Liquid Phase High Pressure Chemistry; Wiley-Interscience: Chichester, UK, 1981; Ch. 2.
10. Klärner, F.-G.; Breitkopf, V. Eur J Org Chem 1999, 2757–2762.
11. Jenner, G.; Papadopoulos, M.; Rimmelin, J. J Org Chem 1983, 48, 748–749.
12. Kiselev, V. D. Kashaeva, E. A.; Konovalov, A. I. Tetrahedron 1999, 55, 1153–1162.
13. George, A. V.; Isaacs, N. S. J Chem Soc, Perkin Trans II 1985, 1845–1848.
14. Grieger, R. A.; Eckert, C. A. J Chem Soc, Faraday Trans I 1970, 66, 2579–2584.
15. McCabe, J. R.; Eckert, C. A. Ind Eng Chem Fund 1974, 13, 168–172.
16. Wurche, F.; Klärner, F.-G. In High Pressure Chemistry; van Eldik, R.; Klärner, F.-G. (Eds.); Wiley-VCH: Weinheim, Germany, 2002; Ch. 2.
17. Jenner, G. J Phys Org Chem 2002, 15, 1–16.
18. El'yanov, B. S.; Gonigberg, E. J Chem Soc, Faraday Trans I 1979, 75, 172–175.

19. Brown, P.; Cookson, R. S. Tetrahedron 1965, 21, 1977–1991.
20. Kiselev, V. D.; Kashaeva, E. A.; Luzanova, N. A.; Konovalov, A. I. Thermochim Acta 1997, 303, 225–228.
21. Rogers, F. E. J Phys Chem 1972, 76, 106–109.
22. Haberfield, P.; Ray, A. K. J Org Chem 1972, 37, 3093–3096.
23. Smith, A. L.; Walter, E.; Korobov, M.; Gurvich, O. L. J Phys Chem 1996, 100, 6775–6780.
24. Ruelle, P.; Farina-Cuendet, A.; Kesselring, U. W. J Am Chem Soc 1996, 118, 1777–1784.
25. Millero, F. J. Chem Rev 1971, 71, 147–176.
26. Markus, Y.; Hefter, G. Chem Rev 2004, 104, 3405–3452.
27. Kumar, A. Chem Rev 2001, 101, 1–19.
28. Kiselev, V. D.; Konovalov, A. I.; Asano, T.; Iskhakova, G. G.; Kashaeva, E. A.; Shihab, M. S.; Medvedeva, M. D. J Phys Org Chem 2001, 14, 636–643.
29. Kiselev, V. D.; Iskhakova, G. G.; Kashaeva, E. A.; Potapova, L. N.; Konovalov, A. I. Russ Chem Bull, Int Ed 2004, 53, 2490–2495.
30. Kiselev, V. D.; Kashaeva, E. A.; Iskhakova, G. G.; Potapova, L. N.; Konovalov, A. I. J Phys Org Chem 2006, 19, 179–186.
31. Grieger, R. A.; Eckert, C. A. Ind Eng Chem Fund 1971, 10, 369–374.
32. Kiselev, V. D.; Kashaeva, E. A.; Shihab, M. S.; Medvedeva, M. D.; Konovalov, A. I. Russ Chem Bull, Int Ed 2000, 49, 1040–1044.
33. Jenner, G. In Organic High Pressure Chemistry, le Noble, W. J. (Ed.); Elsevier: Amsterdam, 1988; Ch. 6.