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[2π+2π]-Cycloaddition of Biadamantylidene to 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione. Effects of Temperature, High Pressure, and Solvent

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Abstract—The effects of temperature, solvent nature, and high hydrostatic pressure on the rate of the reaction of biadamantylidene with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione have been estimated. Significant shielding of the C=C double bond in biadamantylidene is responsible for the high entropy and volume of activation. Quantitative yield of the reaction in the temperature range 25–45°C is related to its exothermicity. The rate of the [2π+2π]-cycloaddition unexpectedly weakly depends on the solvent polarity, which makes it radically different from the [2π+2π]-reaction with tetracyanoethylene.

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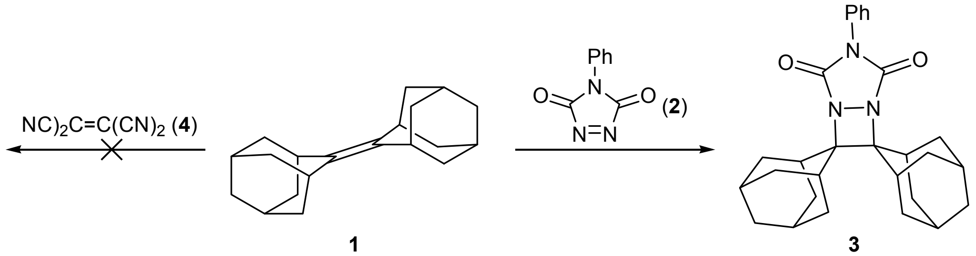
A large number of studies have been performed on [2+2]-cycloadditions with various pairs of substituted ethylenes, where one component exhibits pronounced electron donor properties (vinyl ethers, tetramethoxyethylene, cyclopropyl-substituted ethylenes) and the other is an electron acceptor (di-, tri-, and tetracyanoethylenes) [1–5]. In most publications, an appreciable effect of molecular asymmetry of the donor and acceptor reagents on the reaction rate was noted. Reactions of vinyl ethers with tetracyanoethylene were found to accelerate in polar medium [1, 5, 6]. The stereospecificity of the addition was conserved by about 90%. The reduced stereospecificity in [2+2]-cycloadditions gave grounds to presume that thermal reactions forbidden by the Woodward–Hoffmann orbital symmetry conservation rules involve intermediate formation of zwitterionic species. Huisgen [1] concluded that the rate of zwitterion transformation into cyclobutane derivative is approximately 5 times higher than the rate of its decomposition into initial tetracyanoethylene and vinyl ether. For the reaction of tetracyanoethylene with anethole the rate constant ratio *k*(acetonitrile)/*k*(cyclohexane) is 29000, for the reaction with ethoxyisobutene, 10800, and for the reaction with butyl vinyl ether, 2600. The ratio *k*(MeCN)/*k*(CCl_4) for the reaction of tetracyanoethylene with 3,4-dihydro-2*H*-pyran is 17000 [6]. The observed differences in the rates of [2+2]-cycloadditions with tetracyanoethylene in polar and nonpolar solvents is consistent with the greater stabilization of polar transition state by 5–6 kcal/mol relative to low-polar initial molecules [1, 6].

In the dienophile series 1,1-dicyanoethylene (electron affinity E_a = 1.53 eV), tricyanoethylene (E_a = 2.10 eV), and tetracyanoethylene (E_a = 2.88 eV) [7, 8], the rate of the Diels–Alder reactions with dienes increases in parallel with the electron affinities of dienophiles [8, 9], whereas [2+2]-cycloadditions of the same dienophiles with vinyl ether display the opposite variation of the reaction rate [1]. A strong effect of the alkene asymmetry on the reaction rate was also observed in [2+2]-cycloadditions of tetracyanoethylene to cyclopropyl-substituted ethylene. 1,1-Dicyclopropylethylene turned out to be more reactive by almost 6 orders of magnitude than *cis*- and *trans*-1,2-dicyclopropylethylenes [3, 4]. The strong influence of solvent on the rate of reactions involving tetracyanoethylene may be rationalized by significant change of solvation and reactivity of tetracyanoethylene. The rate of the nonpolar Diels–Alder reaction of 9,10-dimethyl-

Scheme 1.



anthracene with tetracyanoethylene increases almost 400-fold in going from weakly polar π-donor alkylbenzenes to chloroform [10].

It seemed reasonable to study the effect of solvent polarity on [2+2]-cycloadditions to 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**2**) which exhibits moderate acceptor properties comparable with those of maleic anhydride [11]. If their is an accessible allylic proton, compound **2** readily reacts with substituted alkenes according to the ene reaction pathway, in contrast to the symmetry-forbidden [2+2]-cycloaddition. The Alder-ene reaction of biadamantylidene (**1**) and triazole **2** is forbidden by Bredt's rule, since double bond migration to the bridgehead carbon atoms in **1** would lead to a high strain energy.

In continuation of our studies of the kinetics and thermochemistry of Diels–Alder and Alder-ene reactions of 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**2**) [12], in the present work we estimated the effects of the solvent nature, temperature, and high pressure on the rate of [2+2]-cycloaddition of biadamantylidene (**1**) to **2** with formation of adduct **3** (Scheme 1) and determined the enthalpies of these reactions and equilibrium constants.

According to [13], the reaction **1** + **2** → **3** in benzene is characterized by an enthalpy of activation of 44.4 kJ/mol and an entropy of activation of –138 J× mol^{-1} K^{-1}. The rate constant at 25°C reported in [13] coincided with our data (Table 1), but the enthalpy and entropy of activation were strongly different. As shown by X-ray analysis [13, 14], the four-membered ring in adduct **3** is appreciably bent due to increased steric hindrances to the approach of molecules **1** and **2** to each other. This is consistent with increased negative entropies of activation in all the examined solvents; furthermore, the free energy of activation is contributed mainly by the entropy term $T\Delta S^{\neq}$ (Table 1).

Unlike [2+2]-cycloaddition reactions with tetracyanoethylene (**4**), the rate of which increases by 3–4 orders of magnitude in going from nonpolar solvents to acetonitrile, variation of the rate of the reaction **1** + **2** → **3** in the examined solvents by almost 3 orders

Table 1. Rate constants k_2 (L mol^{-1} s^{-1}), enthalpies $\Delta H^{\neq}$ (kJ/mol), entropies $\Delta S^{\neq}$ (J mol^{-1} K^{-1}), and Gibbs energies of activation $\Delta G^{\neq}$ (kJ/mol, 25°C) for the reaction **1** + **2** → **3** in different solvents

Solvent	ε^{a}	k_2 (25°C)	k_2 (35°C)/k_{rel}	k_2 (45°C)	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	$\Delta G^{\neq}$
Ethyl acetate	6.0	0.00118	0.00191/1	0.00309	35.4	182	89.6
1,4-Dioxane	2.2	0.00138	0.00232/1.2	0.00353	35.0	182	89.2
Benzene	2.3	0.00641	0.00909/4.7	0.134	26.6	198	85.6
		0.00640^{b}	–	–	44.4^{b}	138^{b}	85.5^{b}
Acetone	20.7	–	0.00929^{c}/4.9	–	–	–	–
Dimethylformamide	36.7	–	0.0170^{d}/8.9	–	–	–	–
Toluene	2.3	0.0175	0.0236/12.3	0.0343	24.0	198	83.0
Acetonitrile	37.5	0.0716	0.111/58.1	0.156	28.3	172	79.5
1,2-Dichloroethane	10.3	0.407	0.577/302	0.785	23.4	175	75.5
Chloroform	4.6	1.46	1.78/932	2.27	14.9	192	72.1

[a] Dielectric permittivity [15].
[b] Data of [13].
[c] Calculated with correction for the reaction of **2** with acetone, which contributes ~10% to the overall rate.
[d] Calculated with correction for the reaction of **2** with DMF, which contributes ~20% to the overall rate.

Table 2. Experimental ($\Delta V^{\neq}_{\text{exp}}$, cm^3/mol) and corrected ($\Delta V^{\neq}_{\text{corr}}$, cm^3/mol) volumes of activation for the reaction **1** + **2** → **3** in toluene and ethyl acetate at 25°C

Solvent	k(1000 bar)/k(1 bar)	$d\ln k_p/d_r$, 1 bar	$-\Delta V^{\neq}_{\text{exp}}$	$\beta_T RT$[a]	$-\Delta V^{\neq}_{\text{corr}}$
Toluene	6.45	0.00214	53.1±1.4	2.3	50.8±1.4
Ethyl acetate	7.90	0.00238	58.8±1.5	3.0	55.8±1.5

[a] Compressibility coefficients: toluene, 91.9×10^{-6} bar^{-1}; ethyl acetate, 120×10^{-6} bar^{-1} [17].

of magnitude is not determined by solvent polarity. The rate constants in benzene, acetone, dimethylformamide, and acetonitrile are related as 1:1:1.9:12.2. Considerable increase of the reaction rate in 1,2-dichloroethane and chloroform is likely to result from hydrogen bonding between compound **2** and solvent molecules, as noted for a number of Diels–Alder and Alder-ene reactions with **2**.

We previously found [16] that the change in entropy of chemical reactions is often proportional to the change in reaction volume. Therefore, increased volume of activation may be expected. The volumes of activation were determined for the reactions in toluene and ethyl acetate from the reaction rates at 1 and 1000 bar (Table 2).

We obtained very high negative values of the volumes of activation for the reaction **1** + **2** → **3** in toluene (–50.8) and ethyl acetate (–55.8 cm^3/mol), which were in agreement with the large negative entropies of activation of this reaction. It seemed reasonable to compare the volumes of activation with the volumes of reaction in these solvents. For this purpose, we determined changes in the densities of solutions and calculated concentrations of adduct **3** in the course of the reaction **1** + **2** → **3**, which were substituted into Eq. (12) (see Experimental).

By two measurements for the reaction in toluene we obtained:

(1) $c_{02} = 5.00\times10^{-3}$ M, $c_{01} = 2.46\times10^{-2}$ M:

$$d^{-1} = -(0.04240\pm0.00020)\,c_3 + (1.1574369\pm0.0000004);$$
$$R^2 = 0.9994;\ \Delta V_r = -36.6\ \text{cm}^3/\text{mol};$$

(2) $c_{02} = 2.02\times10^{-2}$ M, $c_{01} = 5.03\times10^{-2}$ M;

$$d^{-1} = -(0.04393\pm0.00025)\,c_3 + (1.1544040\pm0.0000032);$$
$$R^2 = 0.9990;\ \Delta V_r = -38.0\ \text{cm}^3/\text{mol};$$
$$\Delta V_r(\text{av.}) = -37.3\pm0.7\ \text{cm}^3/\text{mol};$$
$$\Delta V^{\neq}_{\text{corr}}/\Delta V_r = -50.8/{-37.3} = 1.36.$$

By two measurements for the reaction in ethyl acetate we obtained:

(1) $c_{02} = 1.50\times10^{-2}$ M, $c_{01} = 6.37\times10^{-2}$ M;

$$d^{-1} = -(0.04064\pm0.00028)\,c_3 + (1.1136663\pm0.0000013);$$
$$R^2 = 0.9991;\ \Delta V_r = -36.5\ \text{cm}^3/\text{mol}.$$

(2) $c_{02} = 5.35\times10^{-3}$ M; $c_{01} = 6.37\times10^{-2}$ M;

$$d^{-1} = -(0.04277\pm0.00047)\,c_3 + (1.114418\pm0.0000008);$$
$$R^2 = 0.9976;\ \Delta V_r = -38.4\ \text{cm}^3/\text{mol};$$
$$\Delta V_r\ (\text{av.}) = -37.5\pm0.8\ \text{cm}^3/\text{mol};$$
$$\Delta V^{\neq}_{\text{corr}}/\Delta V_r = -55.8/{-37.5} = 1.48.$$

The enthalpy of the reaction **1** + **2** → **3** was determined in 1,2-dichloroethane at 25°C by seven double measurements by adding a known volume (V, μL) of a solution of **2**, c_{02} = 0.1455 M, to 25 mL of a solution of **1**, c_{01} 0.0126 M: (1) V_2 = 60, ΔH = –85.2; (2) V_2 = 60, ΔH = –86.0; (3) V_2 = 60, ΔH = –85.5; (4) V_2 = 60, ΔH = –87.4; (5) V_2 = 80, ΔH = –87.0; (6) V_2 = 80, ΔH = –86.7; (7) V_2 = 80 μL, ΔH = –86.0 kJ/mol; ΔH(av.) = –86.3±0.8 kJ/mol. Thus, the heat effect of the [2π+2π]-cycloaddition reaction under study is much smaller than those of the [4π+2π]-, [2π+2π+2π]-, and [2π+2σ+2σ]-additions and ene reaction [12].

The rate constant k_2 (0.43±0.02 L mol^{-1} s^{-1}) for the reaction of **1** (c_{01} = 0.0126 M) with **2** (c_{02} = 4.64×10^{-4} M) in 1,2-dichloroethane was calculated from the curve of heat evolution which is proportional to the concentration of adduct **3**. A similar value (0.407±0.010 L mol^{-1} s^{-1}) was obtained from the rate of variation of the concentration of **2** (Table 1). This means that the rates of the reaction **1** + **2** → **3**, calculated from the change of the concentration of **3** (determined by calorimetry) and of the concentration of **2** (determined by spectrophotometry), are similar. Therefore, the rate of the transformation of possible intermediate to adduct **3** should be higher than the rate of its formation.

The equilibrium constants for the reaction **1** + **2** → **3** were determined in toluene. The following data were obtained: at 70°C: $c_{01} = c_{02}$ = 0.01317 M, $D_{\infty 2}$ = 0.111, $c_{\infty 2}$ = 4.53×10^{-4} M, K_{eq} = 6.2×10^4; at 80°C: c_{01} = c_{02} = 0.01317 M, $D_{\infty 2}$ = 0.165, $c_{\infty 2}$ = 6.73×10^{-4} M, K_{eq} = 2.7×10^4. Then, the enthalpy of the reaction is –81.5 kJ/mol, and the entropy, –145 J mol^{-1} K^{-1}. Fairly close values of the reaction enthalpies in toluene

Table 3. Rate constants k_2 (L mol^{-1} s^{-1}) for the [2π+2π]-cycloaddition of compound **2** with biadamantylidene (**1**) at 35°C, [2π+2σ+2σ]-reaction of **2** with quadricyclane (**5**) at 25°C [18], [2π+2π]-reaction of **2** with 2-chloroethyl vinyl ether (**6**) at 25°C [19]; ene reaction of **2** with 2-methylbut-2-ene (**7**) at 10°C [20]; [4π+2π]-reaction of **2** with anthracene (**8**) at 25°C [21], ene reaction of **2** with norbornene **9** at 40°C accompanied by rearrangement [22], and ene reaction of **2** with *trans*-hex-3-ene (**10**) at 20°C [23] and enthalpies of dissolution of **2** at 25°C ($\Delta_{\text{soln}}H_2$, kJ/mol) [11] in different solvents

Solvent	**2**+**1**	**2**+**5**	**2**+**6**	**2**+**7**	**2**+**8**	**2**+**9**	**2**+**10**	$\Delta_{\text{soln}}H_2$
Tetrahydrofuran	–	0.0382	–	0.060	0.028	0.327	0.0032	6.7
Ethyl acetate	0.00191	0.068	0.014	0.109	0.057	0.312	0.0046	9.0
1,4-Dioxane	0.00232	0.091	–	0.150	0.094	–	–	8.8
Toluene	0.0236	0.282	–	0.64	0.33	0.775	–	18.3
Acetonitrile	0.111	0.916	0.043	0.57	0.32	0.623	–	14.2
Benzene	0.00909	0.417	0.27	1.26	0.52	–	0.0354	20.6
Chlorobenzene	–	0.99	–	2.56	1.01	–	–	21.8
1,2-Dichloroethane	0.577	3.613	0.12	4.9	1.55	–	0.144	21.9
Chloroform	1.78	6.08	0.18	14.3	5.09	3.05	–	24.4
Methylene chloride	–	–	0.13	8.1	–	–	–	–
Dimethylformamide	0.0170	0.162	–	0.077	–	0.453	–	–
Acetone	0.00929	–	0.014	0.106	–		–	–

(–81.5 kJ/mol) and 1,2-dichloroethane (–86.3±0.8 kJ×mol^{-1}) should be noted. The ratio of the entropies of activation and reaction in toluene (–198/–145 = 1.36) is consistent with the ratio of the activation and reaction volumes (–50.8/–37.3 = 1.36±0.06). The calculated equilibrium constant (4.63×10^6) and rate constant for the reverse reaction ($k_1 = 3.78\times10^{-9}$ s^{-1}) at 25°C correspond to almost complete transformation of **1** and **2** into **3**.

We failed to obtain [2+2]-cycloaddition product from biadamantylidene (**1**) and tetracyanoethylene (**4**). The absorbance of the complex of **4** with toluene in a mixture with **1** in 1,2-dichloroethane with addition of toluene did not change over 2 days. However, it is known that 9,10-dimethoxyanthracene reacts with compound **4** at a fairly high rate, but the reaction stops when equilibrium establishes in the system [10]. The available data on the enthalpies of reactions of various dienes with compounds **2** and **4** indicate that the reactions with **4** are less exothermic (by 20–30 kJ/mol) than those with **2** [24]. Assuming ΔH_{r} = –56 kJ/mol and ΔS_{r} = –145 J mol^{-1} K^{-1} for the reaction of **1** with **4**, the conversion should exceed 80–90%. Thus, invariance of the absorbance of a solution of **1**+**4** suggests very low reactivity of **4** toward **1**.

The data in Table 3 show the effect of solvents on the rate of reactions (1)–(6) involving compound **2**. There is proportionality in the solvent effects on the rates of the [2π+2π]-cycloaddition **1** + **2** → **3**, [2π+2π]-reaction of **2** with 2-chloroethyl vinyl ether **6** (R = 0.98), [4π+2π]- and [2π+2σ+2σ]-cycloadditions, and ene reaction. As follows from the slopes of dependences (1)–(6), the change of the ln$k$(**2**+**1**) value for the reaction **1** + **2** → **3** in the examined solvent series is almost twice as large as those for the other reactions, which indicates stronger solvent effect on that reaction. However, this variation is not related to the solvent polarity. The rates of the reaction **1** + **2** → **3** in dimethylformamide and acetone are comparable with the rates in benzene and toluene. Change of the enthalpy of solvation of **2** is not the only factor responsible for the variation of the rate of the reaction **1** + **2** → **3** (7).

$$\ln k(\mathbf{2}+\mathbf{5}) = (0.6464\pm0.0642)\ln k(\mathbf{2}+\mathbf{1}) + (1.4277\pm0.2628);\quad R^2 = 0.9442,\ N = 8; \tag{1}$$

$$\ln k(\mathbf{2}+\mathbf{6}) = (0.4071\pm0.0540)\ln k(\mathbf{2}+\mathbf{1}) - (2.0364\pm0.1968);\quad R^2 = 0.9500,\ N = 5; \tag{2}$$

$$\ln k(\mathbf{2}+\mathbf{7}) = (0.6665\pm0.1527)\ln k(\mathbf{2}+\mathbf{1}) + (1.742\pm0.6358);\quad R^2 = 0.7313,\ N = 9; \tag{3}$$

$$\ln k(\mathbf{2}+\mathbf{8}) = (0.5386\pm0.0982)\ln k(\mathbf{2}+\mathbf{1}) + (0.8989\pm0.4024);\quad R^2 = 0.8575,\ N = 7; \tag{4}$$

$$\ln k(\mathbf{2}+\mathbf{9}) = (0.3204\pm0.0709)\ln k(\mathbf{2}+\mathbf{1}) + (0.6923\pm0.2747);\quad R^2 = 0.8718,\ N = 5; \tag{5}$$

$$\ln k(\mathbf{2}+\mathbf{10}) = (0.5485\pm0.2081)\ln k(\mathbf{2}+\mathbf{1}) - (1.4489\pm0.9430);\quad R^2 = 0.8742,\ N = 3; \tag{6}$$

$$\ln k(\mathbf{2}+\mathbf{1}) = (0.3442\pm0.1133)\Delta_{\text{soln}}H_2 - (9.0405\pm2.0060);\quad R^2 = 0.6486,\ N = 7. \tag{7}$$

EXPERIMENTAL

Biadamantylidene **1** was synthesized from adamantan-2-one according to [25]; it was recrystallized from ethanol and additionally purified by alumina column chromatography using hexane as eluent; mp 181–183°C [25]. 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**2**, 97%; from Aldrich, Germany) was purified by sublimation at 100°C (100 Pa), mp 165–170°C (decomp.) [26]). The purity of **2** was checked by spectrophotometry [12]. Adduct **3** was isolated in quantitative yield, mp 228–230°C (decomp.) [13, 14]); its structure was confirmed X-ray analysis and ^{1}H and ^{13}C NMR [13, 14]. All solvents were purified by known methods [15].

Kinetic measurements. The progress of the reaction was monitored following variation of the absorbance of **2** at λ 530–550 nm (Hitachi-2900 spectrophotometer, Japan). A quartz cell containing 3 mL of a solution of **1** was kept in the cell compartment until temperature equilibration (the temperature was maintained with an accuracy of ±0.1°C), and 100–150 μL of a solution of **2** with a required concentration was injected. The working concentration of **2** was $(4–6)\times 10^{-3}$ M, which was 3–12 times lower than the concentration of **1**, to minimize temperature fluctuations of the reaction mixture.

The stability of compound **2** in all solvents used was checked by measuring variation of its absorbance duering the reaction time. The concentration of **2** in DMF and acetone during the reaction time decreased by 20 and 10%, respectively, which was taken into account while calculating the rate constants. The relative standard deviations for the rate constants were within ±3%, for the enthalpy of activation, ±2 kJ/mol, and for the entropy of activation, ±6 J mol^{-1} K^{-1}.

The reaction **1** + **2** → **3** at elevated pressure was carried out in toluene and ethyl acetate at 25°C using an HP-500 pressure regulator (Japan), a PCI-500 variable-volume quartz cell (Japan), and a SCINCO program-controlled spectrophotometer (Korea). The observed volume of activation ($\Delta V^{\neq}_{\mathrm{exp}}$) for the reaction **1** + **2** → **3** in both solvents was calculated from the rate constants at 1 and 1000 bar using Eq. (8) [27]:

$$[\ln k_p/p](1\ \mathrm{bar}) = (1.15\pm 0.03)\ln[k(1000\ \mathrm{bar})/k(1\ \mathrm{bar})]\times 10^{-3}. \tag{8}$$

The volume of activation was corrected for solvent compressibility [19]:

$$V^{\neq}_{\mathrm{corr}} = \Delta V^{\neq}_{\mathrm{exp}} + \beta_T R\,T, \tag{9}$$

where β_T is the isothermal compressibility coefficient of the solvent.

The ratio of the activation and reaction volumes $\Delta V^{\neq}_{\mathrm{corr}}/\Delta V_{\mathrm{r}}$ was determined by the kinetic method, according to which the volume of reaction was calculated from the dependence of the density of solution on the concentration of adduct **3**. For the reaction **1** + **2** → **3**, the overall volume of a solution containing initial reactants **1** and **2** and adduct **3** may be expressed by Eqs. (10) and (11):

$$V_\tau = V_s + (c_{01} - c_{\mathbf{3},\tau})\,V_{\mathbf{1}} + (c_{02} - c_{\mathbf{3},\tau})\,V_{\mathbf{2}} + c_{\mathbf{3},\tau}\,V_{\mathbf{3}}; \tag{10}$$

$$\begin{aligned} V_\tau &= [V_s + (c_{01}\,V_{\mathbf{1}} + c_{02}\,V_{\mathbf{2}})] + c_{\mathbf{3},\tau}(V_{\mathbf{3}} - V_{\mathbf{1}} - V_{\mathbf{2}}) \\ &= V_{\tau=0} + c_{\mathbf{3},\tau}\Delta V_{\mathrm{r}}; \end{aligned} \tag{11}$$

$$1/d_\tau = 1/d_{\tau=0} + c_{\mathbf{3},\tau}\Delta V_{r\text{–}n}/1000\,d_{\tau=0}. \tag{12}$$

Equation (12) derived from (11) by division by the solution weight is more convenient for measuring the density of the reaction mixture during the reaction. Here, $V_{\tau=0}$ and V_τ are the volumes of the mixture at the initial moment and time τ; V_s is the solvent volume; $V_{\mathbf{1}}$, $V_{\mathbf{2}}$, and $V_{\mathbf{3}}$ are partial molar volumes of compounds **1**, **2**, and **3**, respectively; c_{01}, c_{02}, and $c_{\mathbf{3},\tau}$ are the initial molar concentrations of **1** and **2** and the current concentration of **3**; and ΔV_{r} is the volume of reaction. The current concentration of **3** was calculated from the kinetic data. The current densities of the reaction mixture were measured with an Anton Paar DSA 5000M precision densimeter (Austria) at 25±0.002°C with an accuracy of $\pm 2\times 10^{-6}$ g/cm^3.

The enthalpy of the reaction **1** + **2** → **3** in 1,2-dichloroethane was determined at 25°C using a high-precision TAM III calorimeter with a 25-mL glass isoperibolic calorimetric cell equipped with a stirrer, heater, and thermistor. The cell was charged with a solution of **1** (0.0126 M); after temperature equilibration, it was calibrated by supplying a known amount of heat through the heater. A solution of **2** (0.1445 M) was then added in 60–80-μL portions using an automatic dosing unit. Each next portion was added after a time exceeding the time necessary for the reaction completion by more than 99.9%. The heat effect of the addition of a 0.145 M solution of **2** into pure 1,2-dichloroethane was measured in a separate experiment; it proved to be negligible. Successive measurements gave the following enthalpies of the reaction **1** + **2** → **3** in 1,2-dichloroethane: –85.2, –86.0, –85.5, –87.4, –87.0, –86.0, and –86.7 kJ/mol; average value –86.3±0.8 kJ/mol.

Equilibrium constants. A low-melting tube made of molybdenum glass was soldered to a quartz cell. After loading a solution of compounds **1** and **2** ($c_{01} = c_{02} = 0.01317$ M) in toluene, the tube was sealed. The equilibrium constants were calculated from the absorbance of **2** after heating the cell for 3–4 h in the dark at 70 and 80°C (molar absorption coefficient of **2** at λ 540 nm $\varepsilon = 245$ L mol^{-1} cm^{-1}).

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