

# Kinetics and Thermochemistry of $[2\pi+2\sigma+2\sigma]$ -Cycloaddition of Quadricyclane to Tetracyanoethylene

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**Abstract**—Kinetic data for the unusual  $[2\pi+2\sigma+2\sigma]$ -cycloaddition of quadricyclane to tetracyanoethylene in toluene have been obtained for the first time. The same reaction in 1,4-dioxane appears to be the most exothermic among known cycloaddition reactions. The entropy of activation and reaction volume differ only slightly from the corresponding parameters of conventional Diels–Alder reactions.

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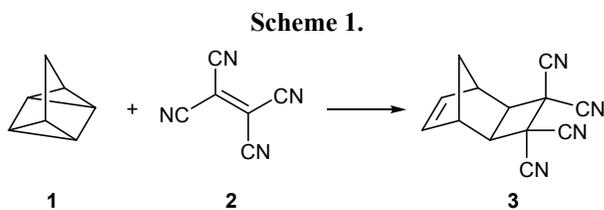
Unusual combination of high strain energy of quadricyclane (**1**, tetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]heptane) (328 kJ/mol [1]) and its thermal stability ( $k_1 = 9.6 \times 10^{-6} \text{ s}^{-1}$  at 140°C [2]) attract a keen interest of researchers. A large volume of data has been accumulated on the synthesis of compound **1** by irradiation of norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) [3], transformation of solar energy into heat [4], and synthesis of  $[2\pi+2\sigma+2\sigma]$ -adducts of quasi-diene **1** with

a broad series of activated dienophiles containing C=C, C≡C, C=O, C=S, C=Si, C=N, and N=N bonds [5]. Polymerization of these adducts may lead to microporous gas-permeable materials [6]. It seems reasonable to compare some characteristics of cyclic quadricyclane isomers (Table 1).

Quadricyclane **1** differs from the other isomers by the low ionization potential and (what is the most important) by sharply increased enthalpy of formation,

**Table 1.** Some properties of cyclic isomers C<sub>7</sub>H<sub>8</sub> at 25°C [1, 5, 7]

Parameter	Quadricyclane	Norbornadiene	Cycloheptatriene	Toluene
<i>d</i> , g/cm <sup>3</sup>	0.9796	0.906	0.9105	0.8669
<i>V</i> , cm <sup>3</sup> /mol	94.1	101.7	101.2	106.3
$\Delta H_{\text{vap}}$ , kJ/mol	37.0	33.6	38.7	38.0
bp, °C	108	89	115.5	110.6
mp, °C	−44	−19	−78	−95
<i>n</i> <sub>D</sub>	1.483	1.470	1.5208	1.4969
<i>MR</i> , cm <sup>3</sup> /mol	35.1	37.3	40.1	40.7
$\Delta H_f$ , kJ/mol:				
gas	339.1	247.6	183.7	50.1
liquid	302.1	214	145.0	12.0
$\Delta\Delta H_f$ , kJ/mol (gas)	289.0	197.5	133.6	(0)
<i>IP</i> , eV	7.40	8.69	—	8.82



which indicates high steric strain of the tetracyclic skeleton. The low ionization potential of **1** is consistent with its high activity in cycloaddition reactions with highly deficient dienophiles [5].  $[2\pi+2\sigma+2\sigma]$ -Cycloaddition of quadricyclane (**1**) with opening of the two cyclopropane rings was reliably proved by X-ray analysis and NMR spectroscopy. The reaction of **1** with tetracyanoethylene (**2**) leads to the formation of *exo*-tricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene-3,3,4,4-tetracarbonitrile (**3**) [8] (Scheme 1).

Analogous cycloaddition reactions have also been reported for strained bicyclo[2.1.0]pentane [9] and bicyclobutane structures [10]. There are many published data [5] on the structure of adducts obtained by  $[2\pi+2\sigma+2\sigma]$ -cycloadditions with quadricyclane (**1**); however, neither rate constants nor activation parameters of these reactions have been reported. In the present work we determined the kinetic and thermochemical parameters of the cycloaddition of **1** with **2** and compared the results with those obtained previously for the reactions of **2** with isomeric nor-

bornadiene and cycloheptatriene, as well as with some 1,3-dienes.

The rate of the reaction **1** + **2** → **3** in toluene was measured at 20 and 40°C. At each temperature, ten kinetic measurements were made in the range of conversions from 0 to 95%; the number of points in the  $\ln D_{\tau} - \tau$  dependences was 237–243 (20°C) and 138–145 (40°C); correlation coefficients 0.9997–0.9999; rate constants  $k_2 = 104.4 \pm 1.5$  and  $178.8 \pm 2.7 \text{ L mol}^{-1} \text{ s}^{-1}$ .

The reaction is favored by increased enthalpy which reflects the energy balance between bond rupture and formation, though this reactivity parameter is not always determining [11]. From the results of four thermochemical measurements for the reaction **1** + **2** → **3** in 1,4-dioxane (Table 2), with account taken of the heat of dissolution of tetracyanoethylene in 1,4-dioxane ( $4.3 \pm 0.2 \text{ kJ/mol}$ ), we calculated the average enthalpy of the reaction in solution:  $\Delta H_r = -236.6 \pm 1.0 \text{ kJ/mol}$ .

The volume of the reaction **1** + **2** → **3** in 1,4-dioxane was determined from the difference in the partial molar volumes (Table 3) which were calculated by the formula:

$$V = [1000(d_0 - d_{r-r})]/m d_0 d_s + M/d_{r-r}$$

where  $M$  is the molecular weight of a compound; for other denotations, see notes to Table 3.

The calculated reaction volume ( $-31.5 \text{ cm}^3/\text{mol}$ ) is typical of most Diels–Alder reactions ( $-25$  to  $-35 \text{ cm}^3/\text{mol}$ ) [12]. Because of the high reaction rate we failed to determine the activation volume which could be calculated from the dependence of the reaction rate on the outer hydrostatic pressure ( $\ln k_2 - P$ ).

The kinetic and activation parameters of this unusual  $[2\pi+2\sigma+2\sigma]$ -cycloaddition of quadricyclane and tetracyanoethylene are as follows:  $k_2 = 104.4 \text{ L} \times \text{mol}^{-1} \text{ s}^{-1}$ ,  $E_a = 20.5 \text{ kJ/mol}$ ,  $\ln A = 13.1$ ,  $\Delta H^\ddagger = 18.0 \pm 1.1 \text{ kJ/mol}$ ,  $\Delta S^\ddagger = -145.0 \pm 4.0 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta G^\ddagger = 60.5 \pm 2.3 \text{ kJ/mol}$ ,  $\Delta H_r = -236.6 \pm 1.0 \text{ kJ/mol}$ . The entropy of activation and pre-exponential factor

**Table 2.** Enthalpies of the reaction **1** + **2** → **3** in 1,4-dioxane at 25°C

Amount of tetracyanoethylene, g	Observed heat effect, J	$\Delta H_r$
0.01391	25.37	-237.9
0.01536	27.90	-237.0
0.01882	34.11	-236.5
0.02663	47.98	-235.1

**Table 3.** Partial molar volumes of quadricyclane (**1**), tetracyanoethylene (**2**), and adduct (**3**) in 1,4-dioxane at 25°C

Comp. no.	$m$ , <sup>a</sup> mol/kg	$d_0$ , <sup>b</sup> g/cm <sup>3</sup>	$d_s$ , <sup>b</sup> g/cm <sup>3</sup>	$V$ , cm <sup>3</sup> /mol
<b>1</b>	0.2225	1.028013	1.026539	96.02
<b>2</b>	0.0155	1.028005	1.028314	105.72
<b>3</b>	0.01803	1.027796	1.028632	170.22

<sup>a</sup> Concentration of solution.

<sup>b</sup>  $d_0$  and  $d_s$  are the densities of the solvent and solution, respectively.

approach the corresponding values for conventional  $[4\pi+2\pi]$  Diels–Alder reactions. In particular, for the fastest reaction of **2** with 9,10-dimethylantracene in toluene at 25°C:  $k_2 = 2810 \text{ L mol}^{-1} \text{ s}^{-1}$ ;  $E_a = 14.4 \text{ kJ/mol}$ ,  $\ln A = 13.7$ ,  $\Delta H^\ddagger = 11.9 \text{ kJ/mol}$ ,  $\Delta S^\ddagger = -138 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta G^\ddagger = 53.0 \text{ kJ/mol}$  [13],  $\Delta H_r = -88 \text{ kJ/mol}$  [11].

Cyclopentadiene ( $k_2 = 478 \text{ L mol}^{-1} \text{ s}^{-1}$ , 1,4-dioxane, 25°C [14],  $\Delta H_r = -113 \text{ kJ/mol}$  [11]) is only four times more reactive than quadricyclane toward tetracyanoethylene.

The rate and heat effect of the reaction **1** + **2** → **3** turned out to be considerably higher than in the reactions of **2** with isomeric norbornadiene ( $k_2 = 1.3 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ , toluene, 35°C [15],  $\Delta H_r = -180 \text{ kJ mol}^{-1}$  [16]) and cycloheptatriene ( $k_2 = 3.68 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ , toluene, 25°C,  $\Delta H^\ddagger = 43.7 \text{ kJ/mol}$ ,  $\Delta S^\ddagger = -145 \text{ J mol}^{-1} \text{ K}^{-1}$  [16]), as well as with cyclohexa-1,3-diene ( $k_2 = 4.92 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ , toluene, 25°C,  $\Delta H^\ddagger = 42.2 \text{ kJ/mol}$ ,  $\Delta S^\ddagger = -128 \text{ J mol}^{-1} \text{ K}^{-1}$  [16],  $\Delta H_r = -130 \text{ kJ/mol}$  [11]) and buta-1,3-diene ( $k_2 = 1.70 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ , methylene chloride, 25°C [14],  $\Delta H_r = -154 \text{ kJ/mol}$  [11]).

Thus, rupture of  $\sigma$ -bonds in the two three-membered rings of quadricyclane (**1**) and subsequent formation of  $\sigma$ -bonds yielding tricyclic adduct **3** is accompanied by high energy gain, which exceeded all known heat effects of the Diels–Alder reactions of 1,3-dienes with tetracyanoethylene. We believe that the high reactivity of quadricyclane in the  $[2\pi+2\sigma+2\sigma]$ -cycloaddition with tetracyanoethylene is determined mainly by huge reduction of its strain energy during the reaction.

## EXPERIMENTAL

Quadricyclane (**1**) was synthesized from norbornadiene as described in [3], dried over metallic sodium, and twice distilled under reduced pressure (600 Pa). The concentration of norbornadiene impurity was determined by titration of a bright red solution of tetracyanoethylene in toluene with a solution of quadricyclane. The rate constants for the reactions of **2** with norbornadiene ( $1.3 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ ) and cycloheptatriene ( $3.7 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ ) are lower by 7 and 5 orders of magnitude, respectively, than the rate constant of the reaction **1**+**2** → **3**. The titration results indicated a  $97 \pm 0.5\%$  purity of **1**. Tetracyanoethylene (Aldrich) was purified by sublimation (100°C, 100 Pa), mp 200–201°C [14]. Adduct **3** had mp 167°C [8].

The rate of the reaction **1** + **2** → **3** in toluene was monitored by the absorption of the  $\pi,\pi$ -complex of **2** with toluene at  $\lambda$  402 nm. The initial concentrations of **1** and **2** were 8–10 and 0.4–0.6 mM, respectively. Under these conditions, the concentration of the  $\pi,\pi$ -complex was proportional to the concentration of tetracyanoethylene. Since the conversion half time did not exceed 0.5 s, the reaction rate was measured by the stopped flow technique (Cary 50 Bio spectrophotometer equipped with an RX 2000 stopped flow unit).

The heat effects were measured according to the procedure described previously [17]. Weighted samples of tetracyanoethylene were placed into stainless steel containers whose ends were hermetically capped with Teflon septa. After temperature equilibration in the calorimeter, the septa were cut off in a quadricyclane solution. In toluene, such measurements were poorly reproducible due to very low solubility of adduct **3** which crystallized on the surface of crystals of **2**. The measurement of heat effects of the reactions in 1,4-dioxane involved no difficulties. The densities of the solvent and solutions were measured at 25°C using a DSA-5000M densimeter.

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