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Assessment of the pre-exponent logarithm for diene synthesis reactions in solution based on the thermal effect

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The pre-exponential factors for diene synthesis reactions in a liquid phase were calculated based on the thermal effects of test reactions.

Previously,[1–5] dealing with cycloaddition reactions, we have developed an approach based on an analysis of interaction of the pre-reaction complex of reagents possessing a rotational momentum of inertia, with electromagnetic waves. Based on this approach, we have developed[2] an isokinetic equation[6] that reflects a linear symbatic relationship between activation parameters, as well as a system of equations[3] analogous to the Evans–Polanyi–Semenov equation that expresses a linear antibatic relationship between the activation energies of exothermic gas-phase reactions and their thermal effects.[7] Furthermore, using the expression for the rotational constant,[8] we obtained a formula for the calculation of the pre-exponential factor (PF).[4,5] This formula is based on the postulate that an electromagnetic wave transfers energy required to overcome the potential barrier.[1,2] In order to meet the energy transfer condition imposed on the electromagnetic wave, it was assumed[4] that its wave number k equals the activation energy $E^{\neq}$ expressed in cm^{-1} in accordance with the relationship[8] 1000 cm^{-1} = 12.5 kJ mol^{-1}.

Based on this approach, we calculated the logarithms of PFs[4] for diene synthesis reactions in gas[4] and liquid phases.[5] The logarithms of PFs for reactions in gas phases were close to experimental data[9] if the value of x, that is, one of the characteristics of the transition state position along the reaction coordinate, was taken into consideration.[2,3] Using the value of x, we obtained the following expression for PF logarithm ($\log A_x$):[4,5]

$$\log A_x = x\log[SNh(M_1 + M_2)/4\pi^2 r^2 M_1 M_2 E^{\neq}], \qquad (1)$$

where r is the distance between the molecules in the complex; M_1 and M_2 are the masses of the molecules that form the complex, kg mol^{-1}; h is the Planck constant (6.62×10^{-34} J s); N is the Avogadro number; and S is the cross-section area of the molecular complex.

Let us represent the cross-section area as a function of squared radius ($S = \pi r^2$), substitute the numeric values of the Avogadro number and the Planck constant into (1), and use the SI atomic mass unit (1.66057×10^{-27} kg)[10]:

$$\log A_x = x\log[191\times10^{17}(M_1 + M_2)/M_1 M_2 E^{\neq}]. \qquad (2)$$

It is possible to obtain the relationship between thermal effect and activation entropy using a linear combination of the isokinetic relationship and the Evans-Polanyi-Semenov equation. Thus, one can expect a relationship between thermal effect Q and PF. Since thermal effect, like activation energy, is an energy parameter of a reaction, let us use formula (2) with thermal effect instead of activation energy in order to reveal the character of the possible relationship:

$$\log A_x = x\log[191\times10^{17}(M_1 + M_2)/M_1 M_2 Q]. \qquad (3)$$

Using formula (3), we have computed logarithms of PFs for a series of liquid-phase diene synthesis reactions, for which experimental data on thermal effects and PF logarithms are available. These include the diene syntheses of anthracene **1**, tetracene **2**, 5,11-dichlorotetracene **3**, 9-methylanthracene **4**, cyclopentadiene **5**, pentacene **6** and 2,5-diphenylisobenzofuran **7** with fumarodinitrile **8**, *N*-phenylmaleinimide **9**, maleic anhydride **10**, tetracyanoethylene **11**, *N*-(*p*-nitrophenyl)arylmaleinimide **12**, methyl acrylate **13** and dicyanoacetylene **14** in benzene **15**,

Table 1 Topological index values for reagent and adduct molecules.

Dienophile	Diene						
	1, $W = 395$	**2**, $W = 803$	**3**, $W = 993$	**4**, $W = 454$	**5**, $W = 21$	**6**, $W = 1458$	**7**, $W = 1143$
8, $W = 64$	841	1439	1629	—	—	2235	
9, $W = 302$	—	2634	2978	1941	437	—	
10, $W = 58$	—	—	—	964	—	2337	
11, $W = 221$	—	2076	2364	—	—	—	
12, $W = 566$	—	—	—	—	878	—	
13, $W = 41$	—	—	—	—	—	—	1789
14, $W = 73$	—	—	—	—	—	—	1822

Table 2 Activation energies, thermal effects, L_i parameters and x values.

Diene	Dieno-phile	Solvent	E/ kJ mol^{-1}	Q/ kJ mol^{-1}	L_2	L_3	x
1	**8**	**16**	65[12]	90[19]	1.7253	1.4973	0.5607
2	**8**	**17**	57[12]	110	1.7544	1.4018	0.4715
2	**9**	**17**	52[13]	126[19]	3.4719	1.7844	0.6375
2	**11**	**15**	39[12]	97[19]	2.6774	1.6018	0.5379
3	**8**	**16**	60[12]	92	1.5798	1.3342	0.4875
3	**9**	**17**	50[13]	107[19]	3.4872	1.7422	0.6666
3	**11**	**15**	41[12]	78[19]	2.6536	1.5594	0.5947
4	**9**	**19**	56[14]	114[19]	3.3643	1.8750	0.6919
4	**10**	**15**	56[15]	101[19]	1.8785	1.5248	0.5190
5	**9**	**19**	34[16]	142[19]	0.7274	1.2232	0.2106
5	**12**	**19**	30[16]	140[19]	1.2026	1.3079	0.2600
6	**8**	**18**	40[12]	129	1.5717	1.2919	0.3450
6	**10**	**17**	41[17]	132[19]	1.7827	1.3344	0.3707
7	**13**	**20**	48[18]	85[18]	1.5604	1.3107	0.4525
7	**14**	**20**	27[18]	129[18]	1.5401	1.3094	0.2879

chlorobenzene **16**, toluene **17**, mesitylene **18**, 1,4-dioxane **19** and 1,2-dichloroethane **20**.

The values of x were calculated from the equation[3]

$$x^3 + x\sqrt{(E^{\neq}L_2L_3)/Q} - (E^{\neq}L_2L_3)/2Q = 0. \qquad (4)$$

Parameters L_2 and L_3 were calculated from the formulas[3]

$$L_2 = \sqrt[3]{W_{\text{products}}} - \sqrt[3]{W_{\text{reactants}}};\quad L_3 = \left(\sqrt[3]{W_{\text{products}}}\right)^2 / \left(\sqrt[3]{W_{\text{reactants}}}\right)^2, \qquad (5)$$

where $W_{\text{products (reactants)}}$ are the values of Wiener topological index[11] for the product and reagent molecules, respectively.

Table 1 lists the values of topological index W for reagent and adduct molecules for the test reactions. Table 2 presents published data on activation energies and thermal effects, as well as parameters L_i and values of x calculated from formula (4). We calculated the thermal effects for diene synthesis reactions of fumarodinitrile with tetracene, 5,11-dichlorotetracene and pentacene using the increment system reported.[20] The calculation formula is as follows:[20]

$$\Delta H_r = -69.04 + \delta h_r^{\text{IBF}} + \delta h_r^{\text{TCE}}, \qquad (6)$$

where ΔH_r is the enthalpy of the reaction, kJ mol^{-1}; δh_r^{IBF} is the reaction enthalpy increment for the diene with respect to 1,3-diphenylisobenzofuran, which equals –27.59 kJ mol^{-1} for tetracene,[20] –9.20 kJ mol^{-1} for 5,11-dichlorotetracene[20] and –46.82 kJ mol^{-1} for pentacene;[20] δh_r^{TCE} is the reaction enthalpy increment for the dienophile with respect to tetracyanoethylene, which equals –13.38 kJ mol^{-1} for fumarodinitrile.[20]

Substitution of the increment values into (6) and analysis of the thermochemical meaning gave the following thermal effects: 110 kJ mol^{-1} for the reaction of fumarodinitrile with tetracene, 92 kJ mol^{-1} for the reaction with 5,11-dichlorotetracene and 129 kJ mol^{-1} for the reaction with pentacene.

Table 3 presents the values required for calculations by formula (3): molecular masses of the addends, kg mol^{-1}; thermal effects in m^{-1}; the value of expression under the logarithm sign (A) in dm^3 mol^{-1} s^{-1}; A logarithm; A logarithm with value x taken into account ($\log A_x$), as well as experimental data on PF logarithms ($\log A_{\text{exp}}$).

Based on data in Table 3, we plotted the calculated PF logarithms *versus* experimental data (Figure 1). The plots have the form of almost parallel straight lines, as suggested by similar slopes of the lines ($\tan\theta$). The relationships are characterised by fairly high correlation coefficients (0.985–0.999) and can be represented by the general formula

$$\log A_x = \log A_{\text{exp}} + B, \qquad (7)$$

where the constant B is 3.57, 1.97, –0.19 or –1.32, which is close to amounts that are multiples of 0.25, namely, 3.50, 2.00, –0.25 and –1.25. We called this trend the multiplicity factor.

Based on the series of numeric coefficients presented, we can assume that the solution of the equations and formulas we use consists of a discrete set of PF values. Discrete sets of states are

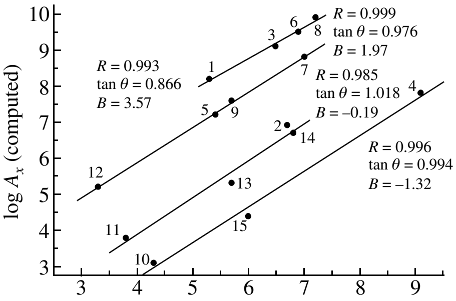

Figure 1 Calculated PF logarithms *vs.* experimental data. The numbers of the points correspond to the data in Table 3.

Table 3 Data for calculation of PF logarithm ($\log A_x$) by formula (3) in comparison with published data ($\log A_{\text{exp}}$).

No.	Diene	Dienophile	Solvent	M_{D}	M_{DPh}	Q/10^5 m^{-1}	A/10^{14} dm^3 mol^{-1} s^{-1}	$\log A$	$\log A_x$	$\log A_{\text{exp}}$
1	**1**	**8**	**16**	0.17824	0.07807	7.20	4.3541	14.64	8.2	5.3[12]
2	**2**	**8**	**17**	0.22830	0.07807	8.80	3.7308	14.57	6.9	6.7[12]
3	**2**	**9**	**17**	0.22830	0.17315	10.08	1.9243	14.28	9.1	6.5[13]
4	**2**	**11**	**15**	0.22830	0.12808	7.76	2.9998	14.47	7.8	9.1[12]
5	**3**	**8**	**16**	0.29728	0.07807	7.36	4.1971	14.62	7.2	5.4[12]
6	**3**	**9**	**17**	0.29728	0.17315	8.56	2.0392	14.31	9.5	6.9[13]
7	**3**	**8**	**15**	0.29728	0.12808	6.24	3.4195	14.53	8.6	7.0[12]
8	**4**	**9**	**19**	0.19227	0.17315	9.12	2.2988	14.36	9.9	7.2[14]
9	**4**	**10**	**15**	0.19227	0.09806	8.08	3.6401	14.56	7.6	5.7[15]
10	**5**	**9**	**19**	0.06611	0.17315	11.36	3.5143	14.55	3.2	4.3[16]
11	**5**	**12**	**19**	0.06611	0.21817	11.2	3.3612	14.53	3.8	3.8[16]
12	**6**	**8**	**18**	0.27836	0.07807	10.32	3.0355	14.48	5.2	3.3[12]
13	**6**	**10**	**17**	0.27836	0.09806	10.56	2.4943	14.39	5.3	5.7[17]
14	**7**	**13**	**20**	0.27032	0.10012	6.8	3.8445	14.58	6.7	6.8[18]
15	**7**	**14**	**20**	0.27032	0.07603	10.32	3.1189	14.49	4.4	6.0[18]

typical of quantum systems. In particular, the energy of rotational molecular motion is a discrete quantity. The concept of rotational motion of molecules in a liquid phase underlies our approach.[1–5] Furthermore, the relationships obtained allowed us to assume that the energy evolved as the thermal effect resulting from the reaction act is directly involved in this act.

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