

A new approach to the evaluation of preexponential factors for cycloaddition reactions in solutions

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A method for the computation of the preexponential factor for diene synthesis reactions in a liquid phase is proposed.

The approach developed for cycloaddition reactions^{1–4} considers the interaction between the pre-reaction complex of reagents, which has a rotational moment of inertia, with electromagnetic waves. Based on this approach, an isokinetic equation was developed³ to reflect a linear symbatic relationship between activation parameters,⁵ and a system of equations was developed,⁴ which is analogous to the Evans–Polanyi–Semenov equation, which expresses a linear antibatic relationship between the activation energies of exothermic gas-phase reactions and their thermal effects.⁶ Furthermore, using the expression for the rotational constant,⁷ a formula for the calculation of the preexponential factor was obtained.⁸ The formula is based on the postulate about the interaction of a molecular complex of reagents, which possesses a rotational momentum of inertia, with an electromagnetic wave that carries energy required for overcoming the potential barrier.³ To fulfill the energy transfer condition imposed on the electromagnetic wave, it was postulated that the wave number k of the electromagnetic wave equals the activation energy E_a with the measurement unit of cm^{-1} in accordance with the following relationship:⁷ $1000 \text{ cm}^{-1} = 12.5 \text{ kJ mol}^{-1}$.

Basing on this approach, we computed the logarithms⁸ of preexponential factors for diene synthesis reactions in a gas phase. In this case, computed preexponential factor logarithms were close to experimental data provided that the x value was taken into account; this value is a characteristic of the position of the transition state on the reaction coordinate.⁴ The final expression that we obtained for preexponential factor logarithm computation ($\log A_x$) was as follows:⁸

$$\log A_x = x \log [SNh(M_1 + M_2)/4\pi^2 r^2 M_1 M_2 E_a], \quad (1)$$

where r is the distance between the molecules in the complex; M_1 and M_2 are the masses of the molecules that constitute the complex; h is the Planck constant, *i.e.*, $6.62 \times 10^{-34} \text{ J s}^{-1}$; N is the Avogadro number, 6.02×10^{23} ; and S is the cross-sectional area of the molecular complex.

Using the well-known formula, let us represent the cross-sectional area as a function of squared radius ($S = \pi r^2$). If this

expression is taken into account, equation (1) takes the form

$$\log A_x = x \log [Nh(M_1 + M_2)/4\pi M_1 M_2 E_a]. \quad (2)$$

Substituting numerical values of the Avogadro number and the Planck constant, and taking into account the value of the atomic mass unit in the measurement units stipulated by the SI system ($1.66057 \times 10^{-27} \text{ kg}$),⁹ transforms equation (2) to

$$\log A_x = x \log [191 \times 10^{17} (M_1 + M_2)/M_1 M_2 E_a]. \quad (3)$$

The use of expression (3) makes computation of the preexponential factor logarithm more convenient since it becomes unnecessary to take into account the distance and cross-section areas, which can depend on the sizes of the molecules that constitute a molecular complex. Hence, an attempt can be made to use equation (3) for evaluating the preexponential factor logarithm for systems that are more complex than those considered previously.⁸

Using equation (3), we calculated the preexponential factor logarithms for a series of liquid-phase reactions of diene synthesis, for which published data regarding the activation energies and preexponential factor logarithms are available. These include diene synthesis reactions of anthracene **1**, tetracene **2**, 5,11-dichlorotetracene **3**, 9-methylantracene **4**, cyclopentadiene **5**, pentacene **6** and 2,5-diphenylisobenzofuran **7** with fumaro-dinitrile **8**, *N*-phenylmaleinimide **9**, maleic anhydride **10**, tetracyanoethylene **11**, *N*-(*p*-nitrophenyl)arylmalenimide **12**, methyl acrylate **13** and dicyanoacetylene **14** in benzene **15**, chlorobenzene **16**, toluene **17**, mesitylene **18**, 1,4-dioxane **19** and 1,2-dichloroethane **20**.

Equation (3) involves the value of x that is calculated using the equation⁴

$$x^3 + x \sqrt{E_a L_2 L_3 / Q} - E_a L_2 L_3 / 2Q = 0, \quad (4)$$

where Q is the heat of reaction, kJ mol^{-1} ;

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

Table 1 Topological indices for reagent and adduct molecules.

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

$W_{\text{products (reactants)}}$ are Wiener topological indices¹⁸ for product and reagent molecules, respectively.

Table 1 shows the topological indices W for reagent and adduct molecules in the reactions considered. Table 2 shows reported activation energies and the heat of reaction with a dimension unit of kJ mol^{-1} , as well as parameters L_i and x calculated by equation (4). We calculated the heat of reaction for diene synthesis of fumarodinitrile with tetracene, 5,11-dichlorotetracene and pentacene using the increment system reported elsewhere.¹⁹

$$\Delta H = -16.5 + \delta h^{\text{IBF}} + \delta h^{\text{TCE}}, \quad (6)$$

where ΔH is the enthalpy of the reaction in question, kcal mol^{-1} ; δh^{IBF} is the increment of the reaction enthalpy for the diene with respect to 1,3-diphenylisobenzofuran, *i.e.*, $-6.6 \text{ kcal mol}^{-1}$ or $-27.6 \text{ kJ mol}^{-1}$ for tetracene,¹⁹ $-2.2 \text{ kcal mol}^{-1}$ or -9.2 kJ mol^{-1} for 5,11-dichlorotetracene¹⁹ and $-11.2 \text{ kcal mol}^{-1}$ or $-46.9 \text{ kJ mol}^{-1}$ for pentacene;¹⁹ δh^{TCE} is the reaction enthalpy increment for the dienophile with respect to tetracyanoethylene, *i.e.*, $-3.2 \text{ kcal mol}^{-1}$ or $-13.4 \text{ kJ mol}^{-1}$ for fumarodinitrile.¹⁹

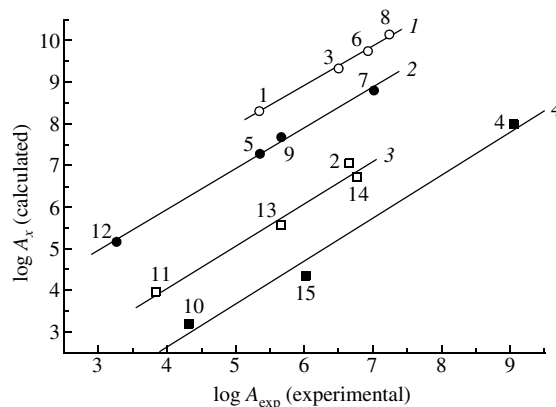
Substituting the increments into (6), converting to SI units and considering the thermochemical meaning gave the following values of the heat of reaction: 110 kJ mol^{-1} for the reaction of fumarodinitrile with tetracene, 92 kJ mol^{-1} for the reaction with

Table 2 Activation energies, heat of reactions, L_i parameters and x values.

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

Table 3 Results of computation of preexponential factor and its logarithm in comparison with published data; starting values for preexponential factor computations.

Entry	Diene	Dienophile	Solvent	$M_D/10^{-3} \text{ kg mol}^{-1}$	$M_{D/Ph}/10^{-3} \text{ kg mol}^{-1}$	$E_a/10^5 \text{ m}^{-1}$	$A/10^{-14} \text{ dm}^3 (\text{mol C})^{-1}$	$\log A$	$\log A_x$	$\log A_{\text{exp}}$
1	1	8	16	178.24	78.07	5.20	6.7656	14.83	8.32	5.34 ¹⁰
2	2	8	17	228.30	78.07	4.56	7.1999	14.86	7.01	6.66 ¹⁰
3	2	9	17	228.30	173.15	4.16	4.6628	14.67	9.35	6.51 ¹¹
4	2	11	15	228.30	128.08	3.12	7.4611	14.87	8.00	9.06 ¹⁰
5	3	8	16	297.28	78.07	4.80	6.4354	14.81	7.22	5.36 ¹⁰
6	3	9	17	297.28	173.15	4.00	4.3640	14.64	9.76	6.92 ¹¹
7	3	8	15	297.28	128.08	3.28	6.5063	14.81	8.81	7.02 ¹⁰
8	4	9	19	192.27	173.15	4.48	4.6797	14.67	10.15	7.24 ¹²
9	4	10	15	192.27	98.06	4.48	6.5651	14.82	7.70	5.67 ¹³
10	5	9	19	66.11	173.15	2.72	14.6773	15.17	3.19	4.32 ¹⁴
11	5	12	19	66.11	218.17	2.40	15.6858	15.20	3.95	3.85 ¹⁴
12	6	8	18	278.36	78.07	3.20	9.7896	14.99	5.17	3.27 ¹⁰
13	6	10	17	278.36	98.06	3.28	8.0303	14.90	5.53	5.67 ¹⁵
14	7	13	20	270.32	100.12	3.84	6.8080	14.83	6.71	6.77 ¹⁶
15	7	14	20	270.32	76.03	2.16	14.9016	15.17	4.37	6.03 ¹⁶

**Figure 1** Plots of computed logarithms of preexponential factor on experimental data. The numbers at the points correspond to data in Table 3. (1) $R = 0.998$, $\text{tg } \theta = 0.95$, $B = 3.24$; (2) $R = 0.998$, $\text{tg } \theta = 0.98$, $B = 2.02$; (3) $R = 0.988$, $\text{tg } \theta = 1.01$, $B = -0.02$; (4) $R = 0.992$, $\text{tg } \theta = 1.03$, $B = -1.52$.

5,11-dichlorotetracene and 129 kJ mol^{-1} for the reaction with pentacene.

Table 3 shows the values required for computing the preexponential factor logarithm by equation (3), *i.e.*, the molecular masses of the addends and the activation energies, as well as the computed values of preexponential factor A , preexponential factor logarithm $\log A$, and preexponential factor logarithm with consideration of the value of x ($\log A_x$). For comparison, Table 3 lists experimental values of the preexponential factor logarithm ($\log A_{\text{exp}}$).

Based on Table 3, we plotted the computed values of preexponential factor logarithm, with the x value taken into account, *versus* experimental data. The plots are presented in Figure 1. These plots consist of a set of nearly parallel straight lines, as follows from the similarity of the slopes of these lines. The relationships are characterised by fairly high correlation coefficients (0.988–0.998) and can be represented by the following general equation:

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

where B takes values of 3.24, 2.02, -0.02 and -1.52 , which are close to values that are multiples of 0.25: 3.25, 2.00, 0.00 and -1.50 . We called this trend the multiplicity factor.

Basing on the series of numeric coefficients provided, it can be assumed that the solution to our equations consists of a discrete set of preexponential factor values. Discrete sets of states are typical of quantum systems. In particular, the energy of rotational motion of molecules is represented by a discrete value. The concept of rotational motion of molecules in the liquid phase underlies our approach^{1,2} and it is also the starting point for the derivation of the formula for preexponential factor computation. The results on preexponential factor calculation that we obtained for reactions in gas and liquid phases are the evidence of the considerable role of rotational motion of molecules in their chemical reactivity.

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