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A new approach to the evaluation of the preexponential factor

Vladimir G. Uryadov* and Evgenii N. Ofitserov

Kazan State Technological University, 420015 Kazan, Russian Federation. E-mail: info@kstu.ru

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A new method for the computation of the preexponential factor for diene synthesis is proposed.

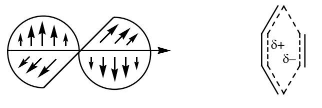
The preexponential factor (PF) in the Arrhenius equation was defined[1] as the number of collisions. The corresponding concept that uses the PF was called the active collision theory, a so-called hard ball model.[2] The latter made it possible to calculate the PF value using the kinetic theory of gases, which considers molecules as rigid spheres that move linearly along straight lines between elastic collisions with each other or with the walls of the vessel containing the gas.[2] However, there are certain contradictions between the collision theory and the kinetic theory of gases. The kinetic theory considers elastic impacts between molecules. The collision theory considers 'special' molecules whose kinetic energies are much higher than the mean value and whose collisions are inelastic. What is more, as a result of collisions, the kinetic energy of linear motion is converted to the potential energy of electron shells, which is accompanied by reorganization of the electron structures of reagent molecules and their conversion into product molecules. The later theory of absolute velocities tried to alleviate the contradictions by entering additional conditions.[1] It has been accepted that transition of an active complex into reaction products does not upset the Maxwell–Boltzman distribution. The effect of the accepted condition was a possibility to express the active complex concentration through concentrations of reagents, energies of the basic state and statistical sums of states of active complexes and reagents.[3] Statistical sums have formed the base of the way to calculate PF in accordance with the theory of active complex.[3] It is possible to calculate the PF values in the theory of active complex by the methods of static thermodynamics on the grounds of function of the distribution of excess energy by the degree of freedom for separate forms of motion.[4] In order to determine the statistical sums, one should know molecular weights, inertia moments, and oscillation frequencies of the initial molecules and the active complex. The statistical sums of rotary motion of the active complex can be calculated only on the ground of the assumption about its geometry,[3] which is believed to be practicable only for small molecules. Calculation of PF also presupposes that on colliding the molecules of reagents will have the spatial orientation required for the reaction process.[3] Such a calculation of PF in the active complex theory does not touch the mechanism of energy transformation, resulting in overcoming the potential barrier.

However, these conditions concerned the probability of a favourable result upon a collision but did not deal with the physical nature of processes that occur during collisions, in particular, the conversion mechanism of the kinetic energy of linear motion into the potential energy of electron shells.

A specific feature of molecules is their quantum nature. Molecules can absorb and radiate electromagnetic waves.[5] The energy transferred by electromagnetic waves can be converted into the potential energy of electronic shells of molecules, kinetic energy of vibrational motion of atoms in a molecule, and energy of rotational motion of a molecule as a whole. In accordance with previous data,[6] we consider the interaction of a rotatory complex of reagent molecules[4] and an electromagnetic wave (Figure 1).

Since a molecular complex formed by reagents is a common system with separated electric charges,[7] let us consider the interaction of an electromagnetic wave with a common supramolecular structure that can undergo rotational motion.[5] An electromagnetic wave is characterised by velocity v, which is determined as the ratio of frequency ω to wave number k:[8]

$$v = w/k. \tag{1}$$



An electromagnetic wave traveling with velocity *v*

A molecular complex with cross-sectional area *S*

Figure 1 Interaction between a traveling electromagnetic wave and a molecular complex.

On the other hand, the vibration frequency of a wave that interacts with a molecular complex can be determined from rotational constant B with dimensionality s^{-1}, which determines the rotational motion energy levels:[5]

$$B = h/8\pi^2 I, \tag{2}$$

where h is the Planck constant equal to 6.62×10^{-34} J s, I is the momentum of inertia of rotational motion, kg m^2.

The frequency of an absorbed electromagnetic wave should match the difference between two consecutive states of rotational motion, which is equal to $2B$ for a linear molecule:[5]

$$w = 2B. \tag{3}$$

The wave number characterises the travel of an electromagnetic wave in space. Since a traveling electromagnetic wave transfers energy required to overcome a potential barrier,[9] it may be assumed that the wave number expressed in cm^{-1} equals the activation energy (E_a) of chemical reaction:

$$k = E_a\ (\mathrm{cm}^{-1}). \tag{4}$$

Then, the expression for the velocity of an electromagnetic wave obtained by substitution of (3) and (4) into (1) has the form

$$v = 2B/E_a. \tag{5}$$

In chemical kinetics, the interaction of two objects is considered as a bimolecular reaction.[1–4] The dimension of the rate constant for a bimolecular reaction is dm^3 mol^{-1} s^{-1} or m^3 mol^{-1} s^{-1}. Let us convert these units as follows:

$$\mathrm{m^3\ mol^{-1}\ s^{-1} = (m^2\ mol^{-1})\times(m\ s^{-1})}. \tag{6}$$

Formula (6) contains two terms: the dimension of one of them is the area of a molecular layer formed by a mole of a compound (m^2 mol^{-1}), while that of the second term is velocity (m s^{-1}). Such a combination suggests an interaction of an electromagnetic wave traveling at velocity v given by equation (5) with a rotating complex, which has an area of S (Figure 1). Then, according to equations (2), (5) and (6), the PF (A) for one molecule should be calculated as:

$$A = Sv = 2BS/E_a = Sh/4\pi^2 IE_a. \tag{7}$$

According to (7), the PF characterising the number of active collisions for one mole should be calculated as:

$$A = SN_A h/4\pi^2 IE_a, \tag{8}$$

where N_A is the Avogadro constant, that is, 6.02×10^{23}.

Hereby PM will have the sense of energy, entering the volume, occupied by one mole, in a unit of time. The momentum of inertia for a linear molecular body is calculated through reduced mass M_{red} by the formula[5]

$$I = r^2 M_{\mathrm{red}} = r^2[M_1 M_2/(M_1 + M_2)], \tag{9}$$

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.

Taking (9) into account, formula (8) takes the form:

$$A = SN_\mathrm{A}h(M_1 + M_2)/4\pi^2r^2M_1M_2E_\mathrm{a}. \qquad (10)$$

For calculation using formula (10) there is no need to know inertia moments by coordinate axes and geometries of the active complex that for large organic molecules will make up an insoluble due to the absence of corresponding physical methods for defining their chemical structure.[3]

However, calculation of PF requires to take into account the existence of the transition state. In the approach developed, there appears the value of ‘x’,[9] characterising the position of transition state on the reaction coordinate.[10] Its role is similar to that of transmittance,[3] which characterises the probability that the system, having reached the transition state, will go through it. With the use of ‘x’, we have taken into account the probability for the transition state to proceed as follows:

– logarithms of the left and right parts of expression (10) were taken;

– the value of the resulting PF logarithm was multiplied by x.

As a result, we obtained the following formula for the PF logarithm, taking into account the position of the transition state along the log A_x reaction coordinate:

$$\lg A_x = x\lg[SN_\mathrm{A}h(M_1 + M_2)/4\pi^2r^2M_1M_2E_\mathrm{a}]. \qquad (11)$$

It is known that molecules necessarily exist in rotational motion when they are in the gas phase;[5] for this reason, we checked the capability of formula (11) for reactions of diene synthesis in the gas phase. We considered gas-phase reactions[8] of buta-1,3-diene **1**, 2-methylbuta-1,3-diene **2**, and cyclopentadiene **3** with ethylene **4** and acrolein **5**.

Calculations by formula (11) require the knowledge of x, which is determined by the formula:[9]

$$x^3 + \mathrm{x}\sqrt{E_\mathrm{a}L_2L_3/Q} - (E_\mathrm{a}L_2L_3)/2Q = 0, \qquad (12)$$

where Q is the thermal effect of a reaction, kJ mol^{-1}, L_2 and L_3 are parameters that quantitatively characterise changes in the structures of molecules due to transition from reagents to products and that are calculated using the values of topologic Wiener index W (see ref. 9) for reagents and products using the formulas:[9]

$$L_2 = \sqrt[3]{W_\mathrm{products}} - \sqrt[3]{W_\mathrm{reagents}}, \qquad (13)$$

$$L_3 = \left(\sqrt[3]{W_\mathrm{products}}\right)^2 / \left(\sqrt[3]{W_\mathrm{reagents}}\right)^2. \qquad (14)$$

Table 1 presents the Wiener topological indices for the molecules of dienes, dienophiles and adducts. Table 2 presents the parameters L_i, activation energies (kJ mol^{-1}), and thermal effects (kJ mol^{-1}). Table 3 shows the molecular masses of the addends, that is, M_1 (diene) and M_2 (dienophile) (g mol^{-1}) and equivalent masses M_eq (kg) for a linear supramolecular structure model (kg) calculated using the mass unit that is equal to 1.66057×10^{-27} kg.[8] The momentums of inertia (I/kg m^2) for intermolecular distance $r = 2$ Å $= 2\times10^{-10}$ m (see ref. 5) and the values of the rotational constant (B/s^{-1}) are also shown in Table 3.

Table 4 presents the values of x, activation energies expressed in m^{-1}, PF values (A/dm^3 mol^{-1} s^{-1}), logarithms of PF corrected for the position of the transition state on the reaction coordinate (log A_x), experimental values of the logarithm PF ‘lg A_exp’ and the values of A_x. In calculations of the PF values, a molecular size on the order of a nanometer[5] and an area of about 10^{-18} m^2 were used. The activation energy in kJ mol^{-1} was converted to m^{-1} by the following relationship:[5] 1000 cm^{-1} = 12.5 kJ mol^{-1}. The values of PF were calculated and converted from SI units (m, mol, s)[8] to units accepted in chemical kinetics (dm^3, mol, s).[1]

Table 4 shows that the majority of calculated values agree with experimental data. The deviations lie within unity on the logarithmic scale or one order of magnitude on the PF scale; this may be regarded as a satisfactory agreement.

Table 1 Topological indices for diene, dienophile and adduct molecules.

Diene	Dienophile	
	4, $W = 2$	**5**, $W = 16$
1, $W = 16$	30	74
2, $W = 26$	—	101
3, $W = 21$	—	91

Table 2 Characteristics of reactions.

Diene	Dienophile	L_2	L_3	E_a	Q
1	**4**	0.4865	1.4057	115.1[11]	166[13]
1	**5**	1.0235	1.7487	82.4[11]	163[13]
2	**5**	1.1810	1.7949	78.2[11]	175[13]
3	**5**	1.1657	1.8220	63.6[11]	122[13]

Table 3 Characteristics of rotational motion.

Diene	Dienophile	M_1	M_2	$M_\mathrm{red}\times10^{25}$	$I\times10^{45}$	$B\times10^{-9}$
1	**4**	54.09	28.05	0.3066	1.2268	6.8413
1	**5**	54.09	56.06	0.4571	1.8284	4.5856
2	**5**	68.12	56.06	0.5107	2.0424	4.1051
3	**5**	66.11	56.06	0.5035	2.0143	4.1666

Table 4 Calculated PF values and original data for its calculation.

Diene	Dienophile	x	$E_\mathrm{a}\times10^{-5}$/m^{-1}	$A\times10^{-12}$	lg A	lg A_x	lg A_exp	$A_x\times10^{-5}$
1	**4**	0.3036	9.21[7]	8.9434	12.9515	3.9	7.5[11]	0.0794
1	**5**	0.4055	6.59[7]	8.3778	12.9231	5.2	6.2[1]	1.5848
2	**5**	0.4138	6.26[7]	7.9005	12.8976	5.3	6.0[11]	1.9953
3	**5**	0.4433	5.09[7]	9.8557	12.9937	5.8	6.2[11]	6.3096

We calculated the PF values for the diene synthesis reaction based on the assumption that a molecular complex between the molecules of a 1,3-diene and an ethylene compound is formed in the gas phase. As a result, a certain agreement between the theory and experimental data was achieved. This agreement allows us to assume that the diene synthesis in the gas phase, like that in solution,[13] occurs *via* a step involving a molecular complex. This pathway of the diene synthesis reaction in the gas phase may result in a similarity of the activation parameters of this reaction in the gas and liquid phases.[11]

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