Mendeleev Commun., 2003, 13(6), 259–260

Relationship between the cycloaddition activation energy and thermal effect in solutions

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10.1070/MC2003v013n06ABEH001729

Based on the concept of the transition state of the reactions in a liquid phase as a Prigogine dissipative structure, the following equation has been derived establishing the relationship between the cycloaddition activation energy and thermal effect in a solution: $(E_aL_2L_3)/Q = Kx^2$.

Beside the fundamental Arrhenius equation, as well as the collision theory and the absolute rate theory,[1] chemical kinetics also deals with empirical relationships, such as the Evans–Polanyi–Semenov equation, which describes a linear relationship between the activation energy (E_a/kJ mol^{-1}) and the thermal effect of reaction (Q/kJ mol^{-1}) for exothermic reactions in a gas phase:[2]

$$E_a = A - BQ \qquad (1)$$

No strict and consistent studies on this subject have been carried out for exothermic reactions in a liquid phase. This may be due to the absence of a simple theoretical apparatus that allows one to analyse experimental data beyond a limited experimental series. Furthermore, there is no general approach to the estimation of the position of a transition state on the reaction coordinate.[1]

Previously, we have suggested the value of x as a quantitative measure for the transition state position on the reaction coordinate.[3] The value of x is based on the concept that the transition state of a reaction in a solution is considered as a Prigogine dissipative structure in which entropy oscillations occur.[4] The quantity x is an exponent of the circular function of the entropy oscillations eigenfrequency.[3] The following equation was suggested for calculating the value of x from kinetic and thermochemical data:[3]

$$x^3 + x\sqrt{(E_aL_2L_3)/Q} - (E_aL_2L_3)/2Q = 0 \qquad (2)$$

The parameters L_2 and L_3 characterise quantitatively changes in the molecular structures on transition from reactants to products. They are functions of the Winer topological index[5] for the product (W_{products}) and reactant ($W_{\text{reactants}}$) molecules:[6]

$$L_2 = \sqrt[3]{W_{\text{products}}} - \sqrt[3]{W_{\text{reactants}}}, \qquad (3)$$

$$L_3 = \left(\sqrt[3]{W_{\text{products}}}\right)^2 \Big/ \left(\sqrt[3]{W_{\text{reactants}}}\right)^2, \qquad (4)$$

Intrinsically, x ranges from zero to unity.[3] Neglecting x^3 in equation (2) as a small term and transforming the remaining part, we obtain the linear relationship between the activation energy and the thermal effect:

$$(E_aL_2L_3)/Q = 4x^2. \qquad (5)$$

Empirical equation (1) suggests antibatic relationship between the activation energy and the thermal effect. On the other hand, equation (5) characterises a symbatic relationship of these parameters provided that x is fixed. The validity of relationship (5) was checked for the diene synthesis of anthracene **1**, 5,11-dichlorotetracene **2**, tetracene **3**, 6,13-dichloropentacene **4** and pentacene **5** with fumarodinitrile **6** and maleic anhydride **7** in chlorobenzene, toluene and mesitylene. The value of x was calculated using equation (2). The values obtained were used to plot the left-hand side of equation (5) on x^2.

The data used for plotting the graphical relationships are listed in Tables 1–4. The resulting plots are demonstrated in Figures 1–3.

The linear relationships presented here are characterised by high correlation factors. The slopes of the straight lines vary and differ from the corresponding factor in equation (5), which is equal to 4. As follows from the plots, the relationship between the activation energy and the thermal effect of cycloaddition in solutions matches simultaneously (i) the experimental data (and hence the Evans–Polanyi–Semenov equation) and (ii) equation (5) only for a specific solvent and a particular multiplier at x^2. Owing to this feature, this multiplier may be regarded as a constant K that characterises the solvent nature. Accordingly, equation (5) takes the form

$$(E_aL_2L_3)/Q = Kx^2 \qquad (6)$$

or

$$L_2L_3/Kx^2 = Q/E_a. \qquad (7)$$

Table 1 Topological index values for the molecules of reagents and adducts.

Dienophile	Diene				
	1, W = 395	**2**, W = 993	**3**, W = 803	**4**, W = 1713	**5**, W = 1458
6, W = 58	881	1701	1511	2629	2337
7, W = 64	841	1679	1439	2523	2235

Table 2 Characteristics of reactions carried out in chlorobenzene.

Diene	Dienophile	E_a	Q	L_2	L_3	x^2
1	**6**	65[7]	91[8]	1.7253	1.4974	0.3069
2	**7**	52[7]	95[8]	1.9027	1.4095	0.2516
2	**6**	60[7]	92[8]	1.6990	1.3614	0.2576
3	**7**	52[7]	113[8]	1.9654	1.4560	0.2288
3	**6**	54[7]	110[8]	1.7544	1.4018	0.2121
4	**7**	50[7]	90[8]	1.7052	1.3018	0.2160
4	**6**	49[7]	87[8]	1.5012	1.2632	0.1904
5	**6**	30[7]	129[8]	1.5717	1.2919	0.0916

Table 3 Characteristics of reactions carried out in toluene.

Diene	Dienophile	E_a	Q	L_2	L_3	x^2
1	**7**	65[7]	94[8]	1.9120	1.5604	0.3381
1	**6**	71[7]	91[8]	1.7253	1.4974	0.3312
2	**7**	58[7]	95[8]	1.9027	1.4095	0.2768
2	**6**	63[7]	92[8]	1.6990	1.3614	0.2688
3	**7**	56[7]	113[8]	1.9654	1.4560	0.2441
3	**6**	57[7]	110[8]	1.7544	1.4018	0.2223
4	**7**	56[7]	90[8]	1.7052	1.3018	0.2386
4	**6**	52[7]	87[8]	1.5012	1.2632	0.2006
5	**7**	41[7]	132[8]	1.7853	1.3351	0.1376
5	**6**	33[7]	129[8]	1.5717	1.2919	0.0998

Table 4 Characteristics of reactions carried out in mesitylene.

Diene	Dienophile	E_a	Q	L_2	L_3	x^2
1	**6**	75[7]	91[8]	1.7253	1.4974	0.3427
2	**7**	70[7]	95[8]	1.9027	1.4095	0.3257
2	**6**	68[7]	92[8]	1.6990	1.3614	0.2862
3	**7**	58[7]	113[8]	1.9654	1.4560	0.2517
3	**6**	63[7]	110[8]	1.7544	1.4018	0.2426
4	**7**	66[7]	90[8]	1.7052	1.3018	0.2753
4	**6**	55[7]	87[8]	1.5012	1.2632	0.2108
5	**6**	40[7]	129[8]	1.5717	1.2912	0.1423

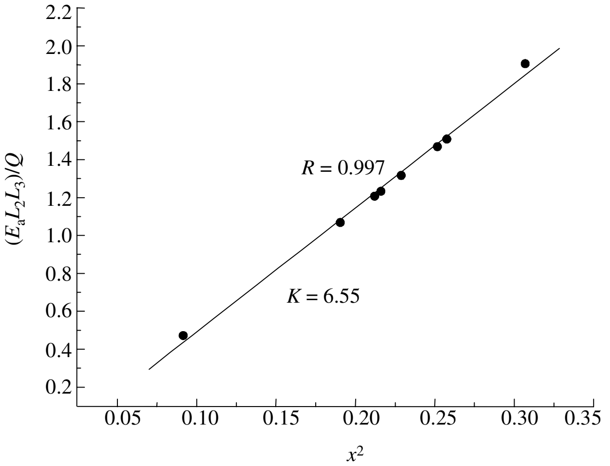

Figure 1 Dependence of the left-hand part of equation (5) on x^2 for reactions in chlorobenzene.

Equations (6) and (7) show that the relationship between the activation energy and the thermal effect of cycloaddition in solution is determined by three factors: the change in the molecular structures on the conversion of the reactants into the products, the solvent nature and the position of the transition state on the reaction coordinate. A certain combination of these factors may result in a relationship similar to equation (1).

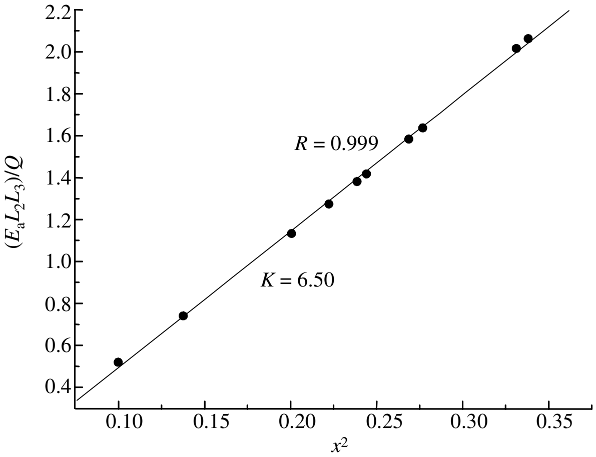

Figure 2 Dependence of the left-hand part of equation (5) on x^2 for reactions in toluene.

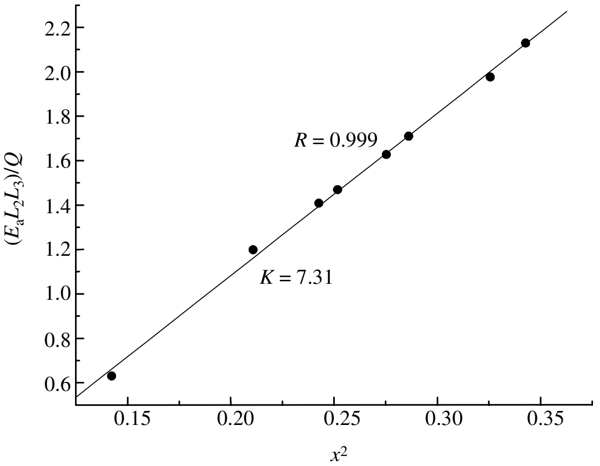

Figure 3 Dependence of the left-hand part of equation (5) on x^2 for reactions in mesitylene.

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Received: 25th February 2003; Com. 03/2055