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A SACM STUDY OF THE CROSS-COMBINATION RATIO OF RATE CONSTANTS

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An analysis of the cross-combination ratio of the rate constants ϕ in terms of the statistical adiabatic channel model allows to factorize ϕ into two contributions: one due to the motion along the reaction coordinates and another due to the reaction transitional modes. ϕ for the CH_3/CCl_3 , $\text{CH}_3/\text{C}_2\text{H}_3$, $\text{CH}_3/\text{C}_3\text{H}_5$, $\text{CH}_3/\text{C}_2\text{H}_5$ and $\text{C}_2\text{H}_5/\text{C}_3\text{H}_5$ radical pairs were calculated.

INTRODUCTION

The cross-combination ratio of the rate constants for the A/B radical pair is defined as $\phi = k_{AB}/(k_{AA}k_{BB})^{1/2}$ [1, 2]. In the cases in which the recombination and disproportionation pathways contribute simultaneously to the reaction, the sum of both rate constants is accounted for in the expression of ϕ . For a variety of hydrocarbon radical reactions ϕ is close to 2 (the so-called geometrical mean rule) [1, 2]. The simple hard-sphere collision theory gives $\phi_{\text{HS}} = 2$ when both the masses and the collision diameters of the reacting radicals are equal and no activation energies are involved [3, 4]. In other conditions the model normally leads to values slightly higher than 2. Clearly this simple model does not account for specific

steric effects: they would yield ϕ values smaller or markedly greater than 2. In these cases, more detailed models taking into account the differences between the angular forces arising from the transitional modes (TMs) of the reactions should be employed. To our knowledge, we present here such a study for the first time. The statistical adiabatic channel model (SACM) [5, 6] was used to calculate ϕ for the CH_3/CCl_3 , $\text{CH}_3/\text{C}_2\text{H}_3$, $\text{CH}_3/\text{C}_3\text{H}_5$, $\text{CH}_3/\text{C}_2\text{H}_5$ and $\text{C}_2\text{H}_5/\text{C}_3\text{H}_5$ radical association pairs and to analyze the dominant potential and molecular features that characterize it.

THEORETICAL FORMALISM AND DISCUSSION

The details of the SACM are well documented, and only a brief outline is given here [5, 6]. The high pressure rate constant for recombination in factorized form is given by [6]

$$k_{\text{rec},\infty} = f_{\text{rigid}} k_{\text{rec},\infty}(\text{PST}) \quad (1)$$

The rigidity factor f_{rigid} accounts for the decrease of $k_{\text{rec},\infty}$ from its phase space limit value, $k_{\text{rec},\infty}(\text{PST})$, due to contributions of the degrees of freedom orthogonal to the reaction coordinate, the TMs. Thus, f_{rigid} can be interpreted as a steric hindrance factor taking into account the anisotropy of the interaction potential. As previously [5, 6], a Morse function with a parameter β calculated with the molecular properties was used for the radial potential while the TMs were modeled by a simple exponential switching function with a global adjustable parameter α . Therefore, $k_{\text{rec},\infty}(\text{PST})$ depends on β , and f_{rigid} on the ratio α/β . $k_{\text{rec},\infty}(\text{PST})$ includes a symmetry number of 1 for $A \neq B$ and 2 for $A = B$, and was evaluated using either diatomic or quasi-triatomic models for the centrifugal potential.

After small corrections of some of the total rate constants for disproportionation processes, the experimental room temperature $k_{\text{rec},\infty}$ values 6.0×10^{-11} [7] ($\text{CH}_3 + \text{CH}_3$), 6.0×10^{-12} [8] ($\text{CH}_3 + \text{CCl}_3$), 3.3×10^{-12} [9] ($\text{CCl}_3 + \text{CCl}_3$), 1.2×10^{-10} [10] ($\text{CH}_3 + \text{C}_2\text{H}_3$), 1.2×10^{-10} [10] ($\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3$), 6.2×10^{-11} [8]

(CH₃+C₃H₅), 2.6x10⁻¹¹ [11] (C₃H₅+C₃H₅), 8.9x10⁻¹¹ [8]
 (CH₃+C₂H₅), 1.9x10⁻¹¹ [7] (C₂H₅+C₂H₅) and 9.5x10⁻¹¹ cm³ mol⁻¹
 s⁻¹ [8] (C₂H₅+C₃H₅) were fitted with eq. 1, using the following
 α/β values: 0.573, 0.447, 0.503, 0.540, 0.599, 0.522, 0.548,
 0.540, 0.463 and 0.524, respectively. From this calculation the
 f_{rigid} values 3.77x10⁻¹, 7.39x10⁻³, 3.10x10⁻², 4.00x10⁻¹,
 6.03x10⁻¹, 1.46x10⁻¹, 1.72x10⁻¹, 3.12x10⁻¹, 1.02x10⁻¹, 2.83x10⁻¹
 were derived. The corresponding $k_{\text{rec},\infty}$ (PST) values can be im-
 mediately obtained via eq. 1. The resulting ratio $\langle \alpha/\beta \rangle = 0.53 \pm$
 0.04 is 13% greater than those obtained in Ref. 6 for a varie-
 ty of triatomic and polyatomic molecules. The differences in
 the α/β values reflect differences in the details of the poten-
 tials and, naturally, inherent experimental errors.

The SACM cross-combination ratio is derived by introducing
 eq. 1 in the expression of ϕ given above, so that

$$\phi = \phi_{\text{rigid}} \phi_{\text{PST}} \quad (2)$$

The factor ϕ_{PST} is defined for the loose rate constants $k_{\text{rec},\infty}$
 (PST), while ϕ_{rigid} includes only the respective f_{rigid} fac-
 tors. Table 1 shows ϕ_{HS} [8], and the ϕ_{rigid} and ϕ_{PST} calculated
 with the above f_{rigid} and $k_{\text{rec},\infty}$ (PST) values. To study the in-
 fluence of the radial potential on ϕ , eq. 3

$$\phi_{\text{PST}} = \phi_{\text{HS}} \left[D_{e,AB} / (D_{e,AA} D_{e,BB})^{1/2} \right]^{1/3} \quad (3)$$

was derived using the attractive part of a Lennard-Jones poten-
 tial. Here D_e denotes the bond dissociation energy. The ϕ_{rigid}
 values were computed with eq. 2. As the results show, the mag-
 nitudes of ϕ_{rigid} and ϕ_{PST} depend on the radial potential con-
 sidered. The Morse potential predicts that the differences be-
 tween ϕ and ϕ_{HS} are due to both factors in eq. 1. Contrarily,
 the Lennard-Jones potential leads to a ϕ_{PST} very similar to
 ϕ_{HS} and, consequently, attributes the observed discrepancies
 only to the relatively hindered angular motion of the radicals.

Table 1

ϕ_{rigid} ϕ_{PST} and ϕ_{HS} ratios for the radical pairs considered

Radical pair	ϕ_{HS}	Morse		Lennard-Jones		ϕ
		ϕ_{rigid}	ϕ_{PST}	ϕ_{rigid}	ϕ_{PST}	
CH ₃ /CCl ₃	2.59	0.0684	6.25	0.159	2.71	0.43
CH ₃ /C ₂ H ₃	2.04	0.839	1.69	0.686	2.04	1.4
CH ₃ /C ₃ H ₅	2.16	0.573	2.73	0.734	2.18	1.6
CH ₃ /C ₂ H ₅	2.06	1.59	1.66	1.26	2.07	2.6
C ₂ H ₅ /C ₃ H ₅	2.09	2.14	2.00	2.06	2.09	4.3

Although an exact analytical expression for ϕ_{rigid} can be derived, we present here, for simplicity, an approximate equation that reproduces the exact values of Table 1 within 10% and provides a clear visualization of the most relevant factors that characterize it. So, for A and B nonlinear, we have

$$\phi_{\text{rigid}} \approx (kT)^{-5} \left[\chi_{\text{AB}} - (\chi_{\text{AA}} + \chi_{\text{BB}})/2 \right] \prod_{i=1}^5 (\gamma_{i,\text{AA}} \gamma_{i,\text{BB}})^{1/2} / \gamma_{i,\text{AB}} \quad (4)$$

The factor $1/\gamma_i = \epsilon_i^{-\chi_i}$ is proportional to the number of adiabatic open channels of the considered TM. The parameters χ_i and the quanta ϵ_i are functions of the potential and the reactant and product properties [5]. Thus, the frequently observed deviations of ϕ from the estimated ϕ_{HS} (or from ϕ_{PST}) can be mainly attributed to the ratio between the number of open channels for the reaction A+B and the geometrical mean of the number of open channels of both self-associations. The SACM ϕ values approach ϕ_{HS} when a Lennard-Jones function is used and a partial compensation of the individual f_{rigid} factors occurs.

Finally, a detailed calculation of ϕ , based either on sim-

plified [6] or better, if available, ab initio potentials [12-14] seems to be preferable. However, in view of the general lack of information and uncertainty of the real potentials, eqs 2 and 3 provide an alternative and simple way to estimate the role the rigidity of the potential surface plays in ϕ .

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