Notes

Proximity and Orientation Effects on the Intramolecular Reaction between a Pair of Terminal Groups Connected by a Poly(methylene) Chain

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Reactions in a system where mutual positions of reactive groups are highly restricted may show various characteristic features. Among these, proximity and orientation effects for two reacting groups are purely physical ones which can be studied in the intramolecular reaction of a model system, such as X–Y-type molecules. A variety of intramolecular reactions in X–Y-type molecules have been reported,[1-9] and the reaction rates are related to the conformations of the polymeric chain connecting the two reactive sites. In some cases, a conformational calculation has been carried out to evaluate the probability of taking favorable conformations for the reaction.[10-19] In most cases, a model of a core-type reaction probability has been adopted for the calculation, where the probability takes a finite value if the separation between the two functional groups is smaller than a critical distance and otherwise vanishes. This model is evidently an oversimplified one, although the dependence on the separation and orientation of the probability in the real system is not known clearly except for a few cases.[17-19] The purpose of this study is to clarify the applicability and the limitation of the core-type model in the simulation of intramolecular reaction of X–Y-type molecules. To this end, an appropriate function which depends upon the separation and the orientation of the two terminal functional groups was considered for the reaction probability, and the probability was averaged over all possible conformations of the intervening polymeric chain. The result was compared with that for the core model.

The model system adopted in this calculation is the intramolecular electron transfer in the αN-$(CH_2)_n$-αN$^-\cdot$ anion radical with n = 3–16, where αN denotes an α-naphthyl group. The rate study of the electron transfer in solution has been reported by Shimada and Szwarc,[4,5] and the simulation based upon the core probability model has been reported by us.[15] In these studies, the frequency of the intramolecular electron transfer has been found to reflect the dynamic flexibility of the poly(methylene) chain.[4-7,15] On the other hand, however, the present calculation is based on the static model and therefore cannot be the exact simulation. In the static model, the electron transfer is assumed to be much slower than the chain motion and the transfer frequency is porportional to the averaged reaction probability over the whole conformational space. Although this choice of the static model makes the comparison of the results calculated for different reaction probabilities easier, the direct comparison with the experimental data is of little value.

According to quantum mechanical theories,[20,21] the probability of electron transfer p in the αN + αN$^-\cdot$ $\rightleftarrows$ αN$^-\cdot$ + αN system is proportional to the square of an overlap integral S^2 for the lowest unoccupied MO of the two α-naphthyl groups, i.e.,

$$p = k'S^2/r^2 \tag{1}$$

where r is the distance between the two α-naphthyl groups and k' is a constant. For the sake of simplicity, the lowest unoccupied MO was substituted by a π orbital located at the center of the naphthyl group. According to Mulliken et al.,[22] the π-type overlap integral is expressed as

$$S = \cos\theta_1 \cos\theta_2\, r^4 \exp(-a'r) \tag{2}$$

where θ_1 is the angle between the directional vector of the first π orbital and a vector connecting the two π orbitals, and θ_2 is for the second π orbital. In eq 2 only the highest order term of r is kept. The exponential parameter a' is related to the Slater's μ value and the Bohr radius.[22] As usual,[23] however, it was regarded as an adjustable parameter in this calculation. The above considerations permit us to derive the following equation for the reaction probability of electron transfer:

$$p = k \cos^2\theta_1 \cos^2\theta_2\, r^6 \exp(-ar)\ (\text{time}^{-1}) \tag{3}$$

The reaction probability at very small r is of no significance, since the two naphthyl groups in the αN-$(CH_2)_n$-αN system cannot be closer than 5 Å due to the constraints of the connecting chain.[15]

In order to compare the transfer frequencies calculated for different types of reaction probabilities, the frequency P of intramolecular electron transfer was divided by the corresponding bimolecular rate constant k_{ex} calculated on the same basis as the intramolecular frequency. The bimolecular rate constant is evaluated by assuming a random distribution in separation and orientation of the two naphthyl groups. The frequency of intermolecular electron transfer P_2 may be expressed as,

$$P_2 = [\alpha\text{N}] \times \int p(\text{no. of molecules in } dr\, d\theta_1\, d\varphi\, d\theta_2)\, dr\, d\theta_1\, d\varphi\, d\theta_2 = [\alpha\text{N}]^2 \int pN_a r^2 \sin\theta_1 \sin\theta_2\, dr\, d\theta_1\, d\varphi\, d\theta_2/2000\ (\text{M time}^{-1}) \tag{4}$$

where N_a is Avogadro's number. The integration with respect to r should be done over $r = r_c$–∞, r_c being a contact distance between two naphthyl groups and assumed to be 4 Å. A small change of r_c did not affect the following discussion. The integration was performed for the following three cases and the bimolecular rate constant $k_{ex} = P_2/[\alpha\text{N}]^2$ was obtained (r, r_0, and r_c are in Å unit).

(1) Core-type reaction probability: $p = k$ ($r \le r_0$) and 0 ($r > r_0$),

$$k_{ex} = 4\pi N_a(r_0^3 - r_c^3)k/3000\ (\text{M}^{-1}\ \text{time}^{-1}) \tag{5}$$

(2) Separation-dependent reaction probability: $p = kr^6 \exp(-ar)$,

$$k_{ex} = 4\pi k N_a I/10^{27}\ (\text{M}^{-1}\ \text{time}^{-1}) \tag{6}$$

$$I = \int_{r=r_c}^{\infty} r^8 \exp(-ar)\, dr = \frac{\exp(-ar_c)}{a} \sum_{s=0}^{8} \frac{8!\, r_c^{8-s}}{(8-s)!\, a^s} \tag{7}$$

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(3) Separation- and orientation-dependent reaction probability: $p = k \cos^2 \theta_1 \cos^2 \theta_2 r^6 \exp(-ar)$,

$$k_{ex} = kN_a(2/3)^2 I/10^{27} \ (M^{-1} \ time^{-1}) \quad (8)$$

Conformations of the αN-$(CH_2)_n$-αN chain were generated by the direct enumeration method as reported before.[15] The methylene chain was treated on the basis of the usual *t-g* rotational isomer model.[24] The rotational states of the penultimate and ultimate C–C bonds, which should be perturbed by the attachment of the bulky naphthyl group, were determined from a semiempirical potential calculation for 1-propylnaphthalene. Intramolecular atomic overlaps were excluded by rejecting conformations having any skeletal carbon atom pairs which are closer than 3.0 Å. For a chain with $n = 16$, the direct enumeration method was impractically time consuming, and the Monte-Carlo method was used instead. In the latter case, a total of 16 000 non-self-intersecting chains were generated. The average reaction probability for all non-self-intersecting conformations was obtained in a usual mannar,

$$P = \langle p \rangle = \sum_i p_i w_i \exp(-E_i/RT) / \sum_i w_i \exp(-E_i/RT) \quad (9)$$

where p_i, w_i, and E_i denote the reaction probability, the weight of rotational states of penultimate and ultimate C–C bonds, and the energy for the ith non-self-intersecting conformation, respectively. A conformational calculation was also made for *trans*-1,4-bis(α-naphthylmethyl)-cyclohexane[6,15] (n = 6c), whose naphthylmethyl groups were attached in equatorial positions.

Figures 1, 2, and 3 present the ratios P/k_{ex} calculated for the three types of reaction probabilities: (1) the core-type probability, (2) the separation-dependent probability, and (3) the separation- and orientation-dependent probability. The comparison of the first model with the latter two models was made by taking the critical distance r_0 as a distance where the value of $r^6 \exp(-ar)$ is about $^1/_{20}$ of the value at $r = r_c$ (= 4 Å). With this choice of r_0, the results obtained by the core-probability model agreed excellently with those for the separation-dependent probability model. The agreement is especially good when a large r_0 value or a small a value was used. An exceptional case is n = 6c, where the core-model with r_0 = 9 Å gives a much smaller value than those expected from the other two models. When r_0 = 7 or 6 Å, the transfer frequency vanishes (see Figures 2 and 3). An inspection of the distribution of r calculated for this molecule[15] revealed that the distance between the two centers of the naphthyl groups is vertually fixed in a small range of r, i.e., in 10–10.5 Å. Hence, in the present calculation where conformations having r larger than 9 Å are cut off, the transfer frequency may be underestimated. The agreement of results calculated by the core model with those by the separation-dependent model justifies the calculations which have been reported for several different systems using the former model.[10-16]

The effect of mutual orientation is evident in the comparison of the separation-dependent probability model with the separation- and orientation-dependent model. The chain length dependences of P/k_{ex} calculated for the two models are virtually the same except for the case of n = 3. Although the consideration of the orientation effect leads to a small increase in the absolute values of P/k_{ex}, the difference is practically unimportant. A decrease in p/k_{ex} at n = 3 for the orientation-dependent model is remarkable. The decrease shows that there are few sandwich-type conformations in the αN-$(CH_2)_3$-αN molecule.

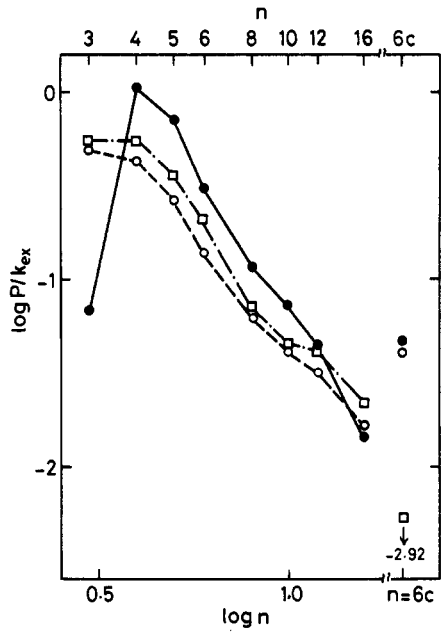

Figure 1. The ratios p/k_{ex} calculated for αN-$(CH_2)_n$-αN$^-$ using three types of reaction probabilities: (1) the core-type probability with r_0 = 9 Å (--□--), (2) the separation-dependent probability with a = 1.5 Å^{-1} (--○--), and (3) the separation- and orientation-dependent probability with a = 1.5 Å^{-1} (—●—). n = 6c indicates *trans*-1,4-bis(α-naphthylmethyl)cyclohexane.

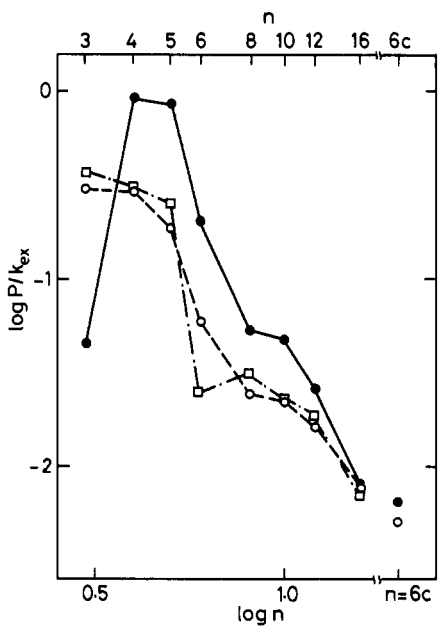

Figure 2. The ratios P/k_{ex} calculated for αN-$(CH_2)_n$-αN$^-$ using three types of reaction probabilities: (1) the core-type probability with r_0 = 7 Å (--□--), (2) the separation-dependent probability with a = 2.0 Å^{-1} (--○--), and (3) the separation-and orientation-dependent probability with a = 2.0 Å^{-1} (—●—). n = 6c indicates *trans*-1,4-bis(α-naphthylmethyl)cyclohexane.

The virtual agreement of the results calculated by the separation-dependent model with the separation- and orientation-dependent one implies that no substantial orientational correlation exists between two terminal functional groups connected by methylene chains longer than n = 3. This finding justifies the simulations of the intramolecular reactions without taking the orientation effect into account.

Similar calculations were carried out for PI$(CH_2)_n$PI, n = 3–16, and PI$(CH_2CH_2O)_mCH_2CH_2$PI, m = 1–4, systems,[15] where PI denotes a phthalimide group. Conclu-

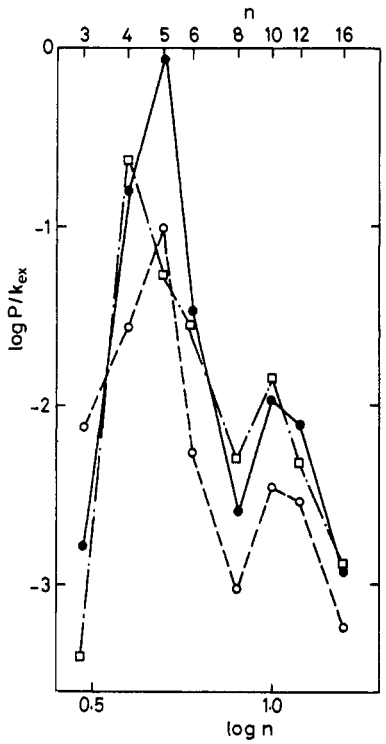

Figure 3. The ratios P/k_{ex} calculated for αN-$(CH_2)_n$-αN$^-$· using three types of reaction probabilites: (1) the core-type probability with r_0 = 6 Å (···□···), (2) the separation-dependent probability with a = 4.0 Å^{-1} (--○--), and (3) the separation- and orientation-dependent probability with a = 4.0 Å^{-1} (–●–).

sions of these calculations were the same as the present study, indicating that a small change in the structure of terminal groups or the connecting chain may not affect the orientational constraint for the terminal groups.

The results of the present calculation showed that the proximity and orientation constraints are not serious in the intramolecular reaction on a poly(methylene) chain and the reaction can be adequately treated with the core-type reaction probability. These findings are compatible with the fact that calculations based on the core-probability model show good agreement with the experimental data.[11-16] In other words, the experimental data of the intramolecular reaction may not afford any information as to the orientation dependence of the reaction probability.

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Computer Simulation of the Intramolecular Electron Transfer in $PI(CH_2)_nPI^-$· and $PI(CH_2CH_2O)_mCH_2CH_2PI^-$· Systems

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The end-to-end intrachain reaction of a chain molecule may provide information on the dynamics and the statics of the chain conformation depending upon the activation energy of the reaction.[1] If the activation energy of the reaction is intrinsically low, the intrachain reaction will be controlled by the diffusion process of two terminal reactive groups approaching each other.[2-6] In the previous paper, we reported a study on the frequency of intramolecular electron transfer in αN-$(CH_2)_n$-αN$^-$·, where αN denotes an α-naphthyl group.[7-9] The frequency was considered as that of the exchange between the favorable conformation for the electron transfer and the unfavorable ones and was calculated as the ratio of the static probability of finding the chain molecule in favorable conformations to the mean lifetime of the favorable conformations. Good agreement between calculated and experimentally obtained results was observed when the favorable conformations for electron transfer were assumed to have end-to-end distances, r, shorter than a critical distance r_0 (r_0 was 8 Å). The good applicability of the dynamic model to the real system prompted us to simulate the frequency of intramolecular electron transfer in $PI(CH_2)_nPI^-$· and $PI(CH_2CH_2O)_mPI^-$· systems, where PI denotes an *N*-phthalimide group.[10] As the chain length dependences of the electron transfer frequency in these three systems are substantially different, the simulation is expected to give an insight into the static and dynamic behaviors of chain conformations.

Hence, conformational calculations of poly(methylene) and poly(oxyethylene) chains were carried out, the structure of the PI group being explicitly taken into consideration. The probability $W(r \leq r_0)$ of finding conformations favorable for the electron transfer having

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