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PREDICTION OF SITE SELECTIVITY IN PHOTOCYCLIZATION OF SEVEN MEMBERED RING COMPOUNDS (2):

BACKGROUND INVOLVED IN REACTIVITY INDEX ΔG_{rs} AND COMPARISON WITH THE EMPIRICALLY DEDUCED POLARIZATION MODEL

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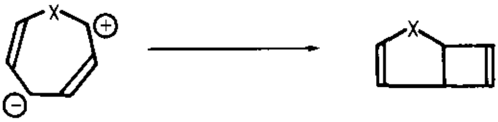
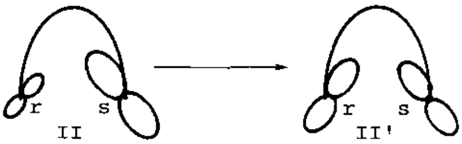
Abstract — The quantitative background of the index ΔG_{rs} proposed by us previously is presented in this paper; a new reactivity index ΔE_{rs} is derived. These indices are compared with the empirically deduced polarization model proposed by Brember et al. Some applications of ΔG_{rs} to the photocyclization of tropolone and azepine derivatives are described.

Previously, we have proposed a new reactivity index ΔG_{rs} which predicts well the site selectivity of photocyclization of cycloheptatrienes.[1] Meanwhile, Brember et al. have proposed an empirically deduced polarization model (I) for predicting the site selectivity of the photocyclization.[2] Very recently, Freestone and Gorman have referred to the ΔG_{rs} index as a theoretical support of their prediction model.[3] However, the background involved in the ΔG_{rs} index does not correspond directly to the polarization model (I). In this paper, we would like to demonsteate this by deriving a new reactivity index ΔE_{rs}. We hope that this provides some insight into the relation between photoreactivities and MO's.

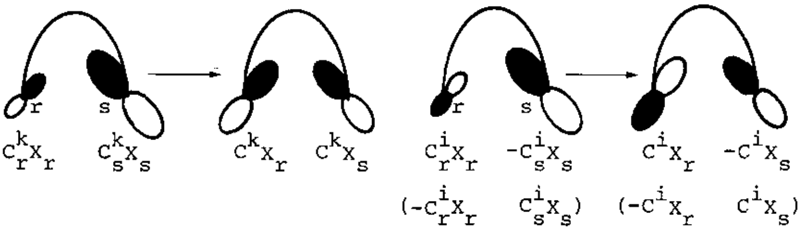


I

As previously reported, we assume that electrons at r and s sites in the orbital system II redistribute when the cyclization proceeds to II'. Let's consider the change of energy due to the transforamtion of the orbital system III to IV, in



II → II'



III → IV V → VI

which the orbitals at r and s sites are of bonding character, $c^k_r \cdot c^k_s > 0$, where c^k_r and c^k_s are LCAO coefficients. If the total electron populations in III and IV are assumed to be constant, $(c^k_r)^2 + (c^k_s)^2 = 2(c^k)^2$, then the energy change (ΔE^k) due to the transformation of the system III to IV is given by eq 1. By the expansion of eq 1 followed by the application of the assumption, eq 2 is obtained, where $\left\langle x_r \middle| H \middle| x_s \right\rangle = \beta$.

$$\Delta E^k = E_{IV} - E_{III} = \left\langle c^k x_r + c^k x_s \middle| H \middle| c^k x_r + c^k x_s \right\rangle$$

$$- \left\langle c^k_r x_r + c^k_s x_s \middle| H \middle| c^k_r x_r + c^k_s x_s \right\rangle \qquad (1)$$

$$= \{2(c^k)^2 - 2c^k_r c^k_s\}\beta$$

$$= (c^k_r - c^k_s)^2 \beta \qquad (2)$$

Similarly, the change of energy (ΔE^i) due to the transformation of the orbital system V to VI, in which the orbitals at r and s sites are of antibonding character, is given by eq 3.

$$\Delta E^i = E_{VI} - E_V = -\{2(c^i)^2 - 2c^i_r c^i_s\}\beta$$

$$= -(c^i_r - c^i_s)^2 \text{ or } -(c^i_s - c^i_r)^2 \beta \qquad (3)$$

In photoreaction of olefines arising from the lowest excited state, the singly occupied MO's correspond to III and V. The orbital system is stabilized when III is transformed to IV, and so ΔE^{k} takes a positive value. On the other hand, the orbital system is destabilized when V is transformed to VI. Thus, ΔE^{i} takes a negative value. Therefore, the stabilization energy ($\Delta E^{II - II'}$) due to the photochemical transformation of II to II' at r and s sites is given by eq 4, from which the ΔE_{rs} index is obtained as shown by eq 5, where $C_r^k \cdot C_s^k > 0$; $C_r^i \cdot C_s^i < 0$.

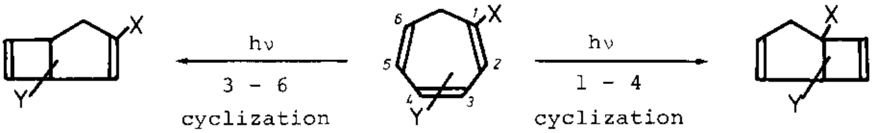
$$\Delta E^{II - II'} = \Delta E^{k} - \Delta E^{i}$$

$$= \{(C_r^k - C_s^k)^2 - (C_r^i + C_s^i)^2\}\beta \qquad (4)$$

$$\Delta E_{rs} = (C_r^k - C_s^k)^2 - (C_r^i + C_s^i)^2 \qquad (5)$$

It is expected that the photocyclization occurs between r and s sites with a larger ΔE_{rs} value. In order to test this we have calculated the ΔE_{rs} values using HMO coefficients[4] for the photocyclization sites in cycloheptatrienes shown by Scheme 1. The ΔE_{rs} values for substituted cycloheptatrienes are presented in Table 1 together with the ΔG_{rs} values.[1] The predicted sites of the cyclization by ΔE_{rs} and ΔG_{rs} agree with each other. Of course, ΔE_{rs} predicts the observed site selectivity of the photoreaction as well as ΔG_{rs} (refer to our previous paper).[1,5]

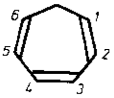
Scheme 1



The ΔG_{rs} index proposed previously by us can be correlated to the index ΔE_{rs} derived in this study. Since C_r^k and C_s^k in eq 5 have the same sign, $|C_r^k - C_s^k|$ is proportional to $|q_r^k - q_s^k|$, where $q_r^k = (C_r^k)^2$ and $q_s^k = (C_s^k)^2$. On the other hand, C_r^i and C_s^i in eq 5 have opposite signs, and so $|C_r^i + C_s^i|$ is proportional to $|q_r^i - q_s^i|$, where $q_r^i = (C_r^i)^2$ and $q_s^i = (C_s^i)^2$. Therefore, eq 5 can be substituted with eq 6 which is the ΔG_{rs} index proposed previously.[1]

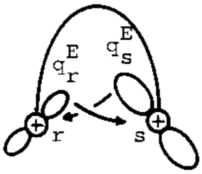
$$\Delta G_{rs} = |q_r^k - q_s^k| - |q_r^i - q_s^i| \qquad (6)$$

Table 1. ΔE_{rs} and ΔG_{rs} values for substituted cycloheptatrienes.[4,5]

	ΔE_{rs}		ΔG_{rs}	
	1 - 4	3 - 6	1 - 4	3 - 6
1 - X	0.019*	-0.017	0.085*	-0.069
2 - X	-0.015	-0.002*	-0.070	-0.004*
3 - X	0.026*	-0.013	0.118*	-0.060
1 - Y	-0.019	0.017*	-0.085	0.069*
2 - Y	0.015*	0.002	0.070*	0.004
3 - Y	-0.026	0.013*	-0.118	0.060*
1 - X ; 4 - Y	0.031*	-0.057	0.142*	-0.185
1 - X ; 3 - Y	-0.006	-0.004*	-0.031	-0.010*
1 - X ; 6 - Y	0.031*	-0.035	0.152*	-0.152
2 - X ; 3 - X	0.012*	-0.015	0.048*	-0.064

* : The predicted site of the cyclization by ΔG_{rs} and ΔE_{rs}.

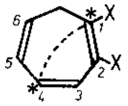
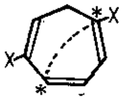
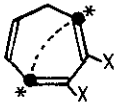
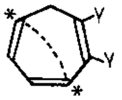
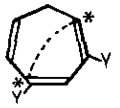
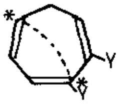
As seen in the derivation of the index, it is obvious that the quantitative basis of the ΔG_{rs} index is not a simple electron-density at r and s sites. The index is derived by considering the energy change of the orbital system at r and s sites in the excited state, and it does not correspond directly to the simple charge interaction between r and s sites in the excited state, which seems to be emphasized in the polarization model (I) by Brember et al.[2] In fact, it has been confirmed that



VII

$$Q^E = (1 - q_r^E)(1 - q_s^E)$$

Table 2. Prediction of the site selectivity for photocyclization of cycloheptatriens by ΔG_{rs} (or ΔE_{rs}) and by the model I.[1,2]

			
ΔG_{rs} (ΔE_{rs})	1 - 4:	0.018 (0.006)	0.080 (0.007)
	3 - 6:	-0.074 (-0.020)	-0.139 (-0.030)
			
ΔG_{rs} (ΔE_{rs})	1 - 4:	0.048 (0.012)	-0.018 (-0.006)
	3 - 6:	-0.064 (-0.015)	0.074 (0.024)
			
ΔG_{rs} (ΔE_{rs})	1 - 4:	0.129 (0.027)	-0.048 (-0.012)
	3 - 6:	-0.113 (-0.024)	0.064 (0.015)

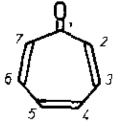
----: Predicted site by ΔG_{rs} (ΔE_{rs}). *: Predicted site by the model I.
● : Observed site.

the netcharge interaction (Q^E) in the excited state between r and s sites in cycloheptatrienes does not predict the observed site selectivity. A model for this calculation is shown by VII, where q_r^E and q_s^E indicate the charge density at r and s sites in the lowest excited state of olefines.

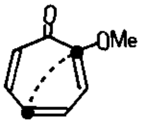
Apart from the arguments of the background of these two prediction models, it is interesting that the predicted sites of the photocyclization in cycloheptatrienes shown in Scheme 1 both by ΔG_{rs} (or ΔE_{rs}) and the polarization model (I) agree well each other. Some examples are presented in Table 2, where X and Y represent the electron-donating and electron-withdrawing groups respectively, and the predicted site of the cyclization by the model I and ΔG_{rs} (or ΔE_{rs}) are shown by the asterisk and dotted line resepctively, together with the ΔG_{rs} (or ΔE_{rs}) values calculated from the HMO coefficients. Among them, the cyclization site indicated by the black circle in the table is observed site in the photocyclization of 2,3,7,7-tetramethylcycloheptatriene.[6] The good agreement of both predictions is rather surprising.

In order to examine further applicability of the index ΔG_{rs}, we have extended our studies to tropolone derivatives. In 1961, Dauben, Koch, Chapman, and Smith re-

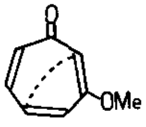
Table 3. Prediction of the site selectivity in photocyclization of tropolone derivatives by the ΔG_{rs} index.

	ΔG_{rs}		Exp.
	2 - 5	4 - 7	
2 - X	0.076 (0.107)	0.024 (-0.006)	XI[8-10]
3 - X	0.045 (0.000)	0.007 (-0.008)	XII[8-10]
4 - X	0.076 (0.011)	0.063 (0.044)	XIII[8-10]
2 - X; 4 - X	0.072	0.058	XIV[8-10]
2 - X; 5 - X	0.042	0.006	XV[8-10]
2 - X; 5 - Y	0.050	-0.010	XVI[11]
2 - X; 6 - X	0.026	0.035	XVII[8-10]

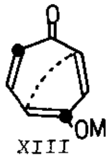
( ): The ΔG_{rs} values for the resonance model.



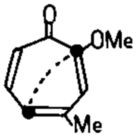
XI



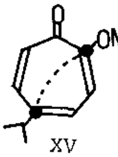
XII



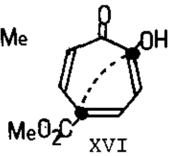
XIII



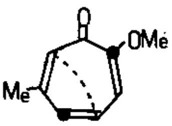
XIV



XV



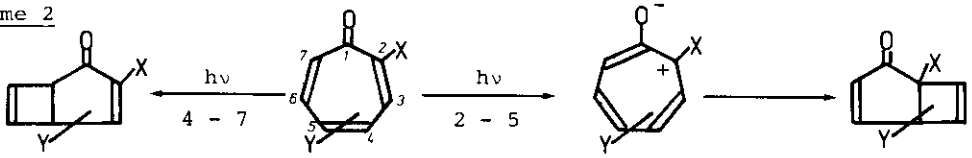
XVI



XVII

ported photocyclization in tropolone derivatives as shown in Scheme 2, in which a strong site selectivity is observed.[7,8] There are two possible reaction sites, C_2-C_5 and C_4-C_7, which undergo the photochemical cyclization to give the bicyclic isomers as shown by Scheme 2. Both of these reaction courses are photochemically allowed from well established orbital symmetry rules. Thus, the site selectivity of the reaction can not be predicted by the orbital symmetry rules. In 1963, Chapman postulated the polar state concept and explained the site selectivity in photocyclization of tropolones on the basis of the dipolar model such as IX.[10] When the polar state (IX) which arises from the excited state of VIII is stabilized

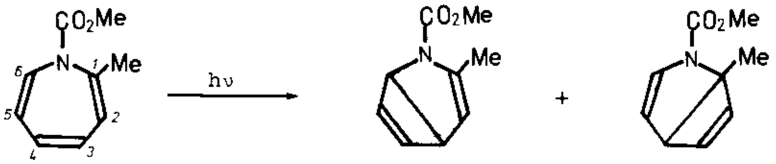
Scheme 2



VIII IX X

by the substituent, the cyclization occurs between C_2 and C_5 to give bicyclic isomer (X). The dipolar model IX seems to have some similiarity with the model I. Interested in this point, we have tested the ΔG_{rs} index to the photocyclization of tropolone derivatives (XI - XVII),[8 - 11] most of which are quoted from a text book edited by Chapman.[10] The ΔG_{rs} values for the π,π^* state of XI - XVII, which were calculated from HMO coefficients computed for the inductive- and resonance-models, are presented in Table 3 together with the experimental observations. In XI - XVII, the dotted lines are the predicted sites by the ΔG_{rs} index, while the black circles are the observed sites of the cyclizations. In general, the differences of the ΔG_{rs} values for the two cyclization sites, the 2 - 5 and 4 - 7 positions, are considerably small in comparison with those in cycloheptatrienes (see Tables 1 and 2). In spite of the small differences, we consider that the reaction occurs at the site with a larger ΔG_{rs} value, and hence we conclude that the agreements of the predictions and observations for XI - XVII are fairly well with some exceptions. The ΔG_{rs} value for XII calculated from the inductive-model predicts the C_2-C_5 cyclization to be preferable, while XII does not photocyclize. The ΔG_{rs} values obtained from the inductive-model do not predict correctly the site selectivity for XIII and XVII.

The strong site selectivity has been observed in the photocyclization of 1-methyl-1H-azepine (XVIII).[12] The calculated ΔG_{rs} values for the 1 - 4 and 3 - 6 cyclizations in XVIII are 0.093 and 0.040 respectively, suggesting XX to be a more preferable product than XIX. This is inconsistent with the experimental observation. Although only a limitted number of tropolone and azepine derivatives are quoted



XVIII XIX XX

(93.5%) (6.5%)

and only the HMO parameters are employed in this study, the discrepancy arising in the photocyclizations of tropolone and azepine derivatives may suggest some limitation of the applicability of the ΔG_{rs} index. We are considering this point further in detail along with a new prediction model.

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