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APPLICATION OF THE ISOSELECTIVE RELATIONSHIP TO DIELS-ALDER REACTIONS

Bernd Giese[+] and Joachim Stellmach[1]
Institute of Organic Chemistry and Biochemistry
Petersenstraße 22, D-6100 Darmstadt, Germany

Otto Exner

Institute of Organic Chemistry and Biochemistry
Czechoslovak Academy of Science, 16610 Prague 6, Czechoslovakia

Abstract: Diels-Alder reactions with "normal" and "reverse electron demand" obey common isoselective relationships (Figure I).

Isoselective relationships (a) are diagnostic tools to distinguish between molecules of different structure.[2] With isokinetic relationships (b) the validity of common reaction mechanisms can be proved.[3,4] If molecules X_1,X_2,X_3.. in competition system Y_1/Y_2 obey an isoselective relationship, reaction series $(X_1,X_2,X_3...)+Y_1$ and $(X_1,X_2,X_3...)+Y_2$ have to follow isokinetic relationships, too.[5,6]

$$\xleftarrow[k_1,\ \Delta H_1^{\ddagger},\ \Delta S_1^{\ddagger}]{\quad Y_1 \quad} X_1,X_2,X_3... \xrightarrow[k_2,\ \Delta H_2^{\ddagger},\ \Delta S_2^{\ddagger}]{\quad Y_2 \quad}$$

$$(\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}) = T_{is} \cdot (\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}) + c \qquad (a)$$

$$\Delta H_1^{\ddagger} = \beta_1 \cdot \Delta S_1^{\ddagger} + c_1 \qquad (b)$$

Therefore reactions of X_1,X_2,X_3... should proceed by a common mechanism if an isoselective relationship exists. We have proved this with dienes 1a-f that react with maleic anhydride and benzoquinone in Diels-Alder reactions with "normal" (1a-d) and "reverse electron demand" (1e-f). If the mechanisms of these reactions are identical[7], dienes 1a-f must obey a common isoselective relationship.

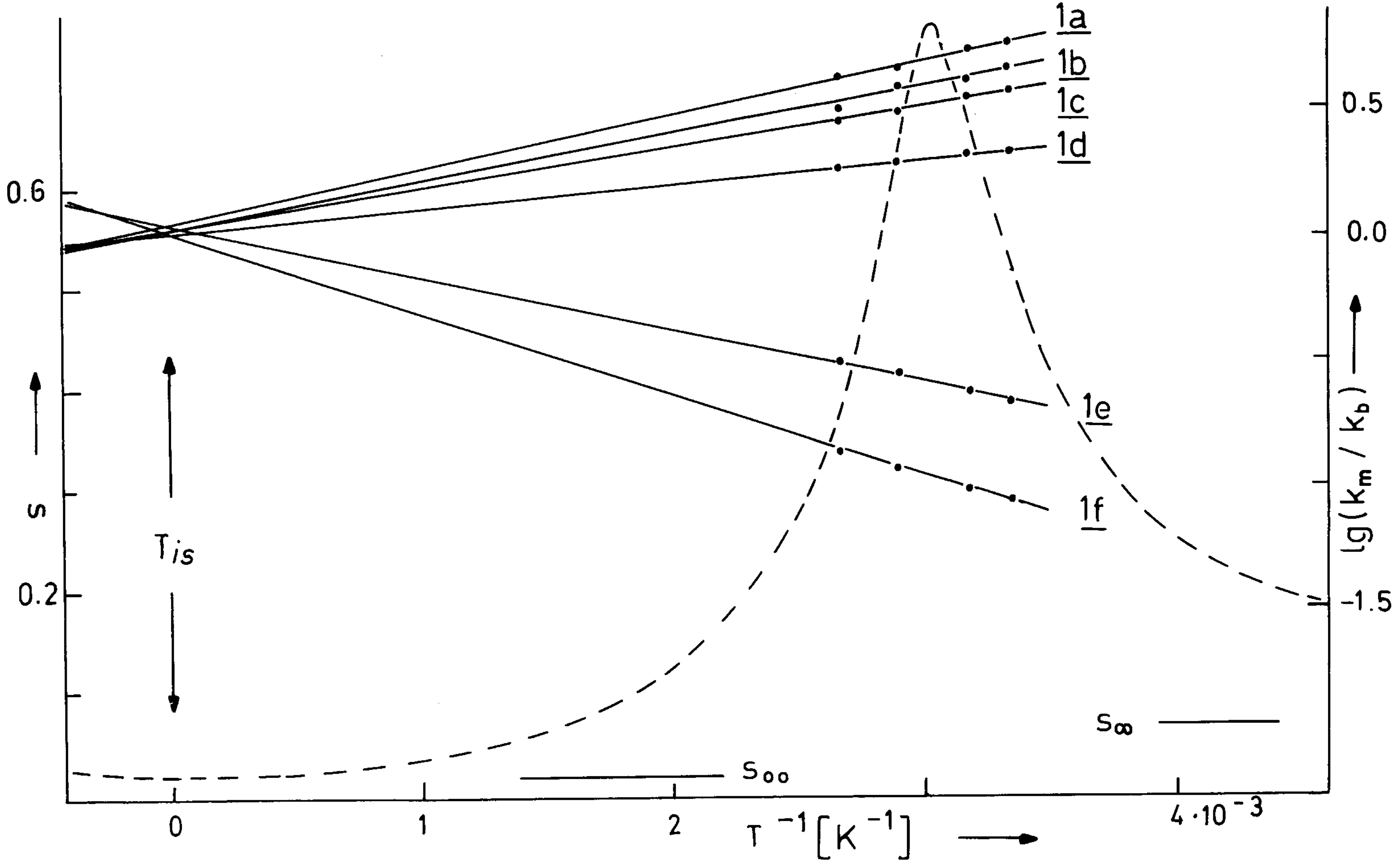
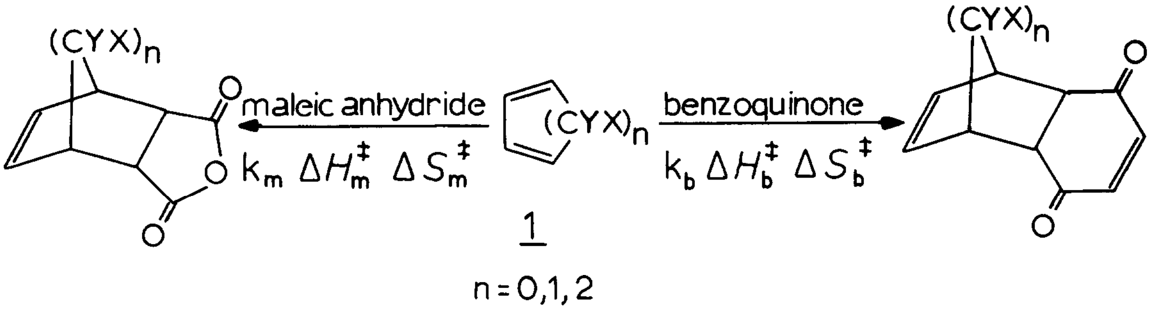


Figure I. Temperature dependence of selectivities $\lg(k_m/k_b)$ and standard deviations s of dienes <u>1a</u>-<u>f</u> in reactions with maleic anhydride/benzoquinone competition system.



Reactions of dienes 1a-f in maleic anhydride/benzoquinone competition system were carried out in dioxane between 298 and 373 K. From competition constants k_m/k_b (see Figure I) activation parameters and standard deviations were calculated (Table I).[4,6] Positive slopes in the Eyring diagram demonstrate "normal electron demand" of dienes 1a-d and negative slopes "reverse electron demand" of dienes 1e-f (Figure I).

Table I

Activation parameters and standard deviations[4,6] of dienes 1a-f in reactions with maleic anhydride/benzoquinone competition system.

	Diene	$\Delta H^{\ddagger}_m$ - $\Delta H_b^{\ddagger}$ kJ·mol^{-1}	$\Delta S_m^{\ddagger}$ - $\Delta S_b^{\ddagger}$ J·mol^{-1}·K^{-1}	s_o	s_{oo}	ψ
1a	Cyclopentadiene	-3.9	1.9	0.0144	0.0121	0.021
1b	Cyclohexadiene	-4.2	-1.5			
1c	Butadiene	-3.4	-0.1			
1d	Methyl-1-butadiene-carboxylate	-1.8	0.6			
1e	Tetrachlorocyclopentadiene	4.7	3.4			
1f	Hexachlorocyclopentadiene	5.4	-1.7			

Because s_{oo} (calculated without additional assumption of the validity of the isoselective relationship) is smaller than s_o (calculated with assumption that the isoselective relationship is valid) and the plot of standard deviation s in Figure I exibits a minimum, the reactions of dienes 1a-f possess a common isoselective relationship.[4,6] The statistical ψ value[8] is 0.021. The standard deviation s_s = 0.0140 (computed with the assumption that $T_{is}=\infty$) shows that these Diels-Alder reactions are isoentropic.

As with isokinetic relationships the existence of isoselective relationships demonstrates common reaction mechanisms, but selectivity measurements have some advantages.

1) Experiments can easily be carried out within large temperature ranges (in these Diels-Alder reactions between 298 and 373 K).

2) With suitable competition systems certain interactions compensate each other (because both maleic anhydride and benzoquinone are planar molecules, steric effects are not important in their competition reactions with 1a-f).

3) Even if concentrations of the responsive molecules X_1, X_2, X_3... are unknown, selectivity measurements can be carried out (dienes 1a-f obey a common isoselective relationship, although the preferential conformation of the butadienes 1c and 1d is s-*trans*).

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References and Notes

1) University Chemical Laboratory, Albertstraße 21, 7800 Feiburg, Germany.

2) B. Giese, *Angew. Chem.* **89**, 162 (1977); *Angew. Chem. Int. Ed. Engl.* **16**, 125 (1977).

3. J.E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York 1963.

4) O. Exner, *Prog. Phys. Org. Chem.* **10**, 411 (1973).

5) B. Giese, *Angew. Chem.* **88**, 161 (1976); *Angew. Chem. Int. Ed. Engl.* **15**, 174 (1976).

6) O. Exner and B. Giese, *Angew. Chem.* **90**, 816 (1978); *Angew. Chem. Int. Ed. Engl.* **17**, (1978).

7) J. Sauer, *Angew. Chem.* **79**, 76 (1967), *Angew. Chem. Int. Ed. Engl.* **6**, 16 (1967)

8) O. Exner, *Collect. Czech. Chem. Commun.* **40**, 2762 (1975).

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