# COMMUNICATIONS TO THE EDITOR

## Cross Interaction Constants in Elimination Reactions

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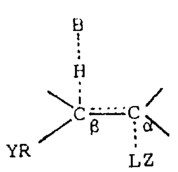
The magnitude of cross interaction constant, $\rho_{YZ}$ in eq. (1), is a quantitative measure of interaction between two substituents Y and Z in the transition state (TS).[1] The $\rho_{YZ}$ values become significant only when both fragments with interacting substituents

$$\log(k_{YZ}/k_{HH}) = \rho_Y\sigma_Y + \rho_Z\sigma_Z + \rho_{YZ}\sigma_Y\sigma_Z \qquad (1)$$

are directly involved in bond-making and/or bond-breaking process in the TS.[1a] For example, in an addition-elimination reaction the $\rho_{YZ}$ will be negligible for Y and Z in the substrate and leaving group, respectively, if the addition step is rate limiting.[1a,2] The intensity of interaction between the two substituents will be influenced by several factors. One such effect has been shown to be the distance involved between the two, and hence the magnitude of $\rho_{YZ}$ can be used as a measure of tightness of bond in the TS.[1,2]

In this report, we show that the magnitude of $\rho_{YZ}$ is strongly influenced and increases dramatically by an extra bridge formation involving a base between the two substituents in a base catalyzed elimination. Thus a distinctively large $|\rho_{YZ}|$ value in the elimination reaction provides strong support for a base catalysis in which a base-bridged TS is formed.

In the E2 $\beta$-elimination,[3] the spectrum of transition state, (I), ranges from one similar to that of $(E1cB)_{irr}$ elimination (E1cB-like) in which $C_\beta$-H bond-breaking has proceeded considerably further than $C_\alpha$-L bond-breaking, to one similar to that of the E1 reaction (E1-like).[3] Intermediate is the symmetrical TS (Sym.).




(I)

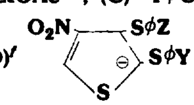
Consideration of the effects of substituents Y and Z leads to the relative size of $\rho$ and $\beta_L$ values as shown in Table 1 for the spectrum of the TS structure (or mechanism). A clear demonstration of such spectrum of the TS variation can be found in the $\beta$-elimination studies involving benzenesulfonates as the leaving group, $LZ = Z\phi OSO_2$. Results of our analysis summarized in Table 2 reveal a perfact parallelism with the predicted trends in Table 1. Note that as bond breaking proceeds further in the TS, the $\rho_Z$ and $-\beta_L$ values increase while $|\rho_{YZ}|$ decreases as predicted from its distance dependence.[1a]

For the reaction C, a base catalyzed bridge structure(II) has been considered as a possible transition state. However if the reaction C proceeded via the hydrogen-bridged structure (II), an abnormally high $|\rho_{YZ}|$ value is expected due to enhanced interaction through an extra bridge between the two substituents Y and Z provided by a catalyzing base molecule; the two substituents can then interact via two paths, and the intensity of interaction ($\alpha|\rho_{YZ}|$) should increase dramatically. Such base-bridged TS can, however, be safely

**Table 1. Spectrum of $\rho$ and $\beta_L$ variation for the $\beta$-elimination mechanisms**

| | | E2 | | | | | |
|---|---|---|---|---|---|---|---|
| | $(ElcB)_{irr}$ | | ElcB-like | Sym.[b] | El-like | | El[c] |
| [a] $\rho_Y$ (positive) | large | > | | IM | | > | ≅0 or small negative |
| $\rho_Z$ (positive) | ≅ 0 | < | | IM | | < | large |
| $\lvert\rho_{YZ}\rvert$ | ≅ 0 | > | | IM | | > | ≅0 |
| $-\beta_L$ | ≅0 | < | | IM | | < | large |

[a] Substituents variation of Y and Z refer to those in (I). [b] For symmetrical E2, the magnitude of various parameters are assigned as intermediate. Since $-\beta_L$ varies from zero to 1.0, IM for this should mean 0.5. $\beta_L$ can be obtained for $^-OSO_2\phi$ by $\rho/\rho_e$ where $\rho_e = 2.94$. (1c). [c] $(ElcB)_{ip}$ and $(ElcB)_R$ mechanisms should also belong to this category.

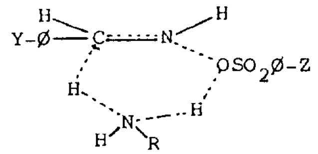
**Table 2. Analysis of $\rho$ and $\beta_L$ parameters for $\beta$-elimination reactions: (A)[c] $Y\phi CH_2CH_2OSO_2\phi Z + t\text{-}BuO^- \rightarrow$; (B)[d] $Y\phi CH_2NHOSO_2\phi Z + \phi CH_2NH_2 \xrightarrow[THF-EtOAc]{H_2O}$; (C)[e] $Y\phi CH_2NHOSO_2\phi Z + \phi CH_2NH_2 \xrightarrow{MeOH}$; (D)[f]** 

**$+ Bu_3N \longrightarrow$**

| | Reaction | | | |
|---|---|---|---|---|
| | [a]A (ElcB-like) | [a]B (Sym.) | [a]C (El-like) | [b]D $(ElcB)_{ip}$ |
| $\rho_Y$ | 2.76 | 0.86 | 0.12 | -0.28 |
| $\rho_Z$ | 1.10 | 1.36 | 1.65 | 3.45 |
| $\rho_{YZ}$ | -0.57 | -0.34 | 0.00 | 0.0 |
| $-\beta_L$ | 0.37 | 0.46 | 0.56 | 0.92 |

[a] Mechanisms in parenthesis are those assigned by the author. [b] Mechanism in parenthesis is that assigned in the original paper. [c] Banger, J.; Cockerill, A.F.; Davies, G.L.O. *J. Chem. Soc.*, (B) 1971, 498. [d] Hoffman R.V.; Belfoure, E.L. *J. Am. Chem. Soc.* 1979, 101, 5687. [e] Hoffman, R.V.; Belfoure, E.L. *ibid.* 1982, 104, 2183. [f] Petrillo, G.P.; Novi. M.; Garbarino, G.; Dell'Erba, C. *J. Chem. Soc., Perkin* **2** 1985, 1741.

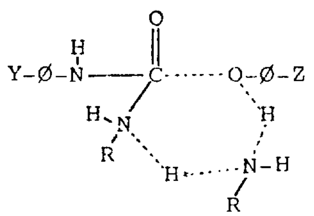
ruled out, since the $\rho_{YZ}$ value of zero was



(II)

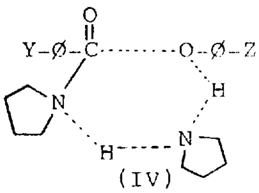
obtained for this reaction as shown in Table 1.

However such mechanism in which the $|\rho_{YZ}|$ values are abnormally large can be found in the base-catalyzed addition-elimination type of the nucleophilic substitution reaction in which elimination is rate limiting.[4] Two examples are: (i)[5] $YC_6H_4NH\ COOC_6H_4Z + RNH_2 \rightarrow YC_6H_4NHCONHR + HOC_6H_4Z$ (2) The $|\rho_{YZ}|$ values for the two reaction paths, i.e., uncatalyzed ($k_2$) and base catalyzed ($k_3$), of this reaction were determined to be 1.02 and 4.00, respectively. For the latter, the TS of the type (III) can therefore be predicted.



(III)

(ii)[6] pyrrolidine + $YC_6H_4COOC_6H_4Z \rightarrow YC_6H_4CONC_4H_8 + HOC_6H_4Z$ (3) The two $|\rho_{YZ}|$ values obtained for $k_2$ and $k_3$ paths of this reaction were 1.76 and 9.33 respectively. The latter base-catalyzed path is predicted to have the base-bridged TS of the type (IV).



We therefore conclude that the cross interaction constants are useful in characterizing an elimination with a base-bridged TS as well as in distinguishing the specific type of TS in the E2 mechanism.

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# Correlation between Catalytic Activity and Acid Strength

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It has been known that the catalytic activity of a catalyst is deeply affected by the method of catalyst preparation and the condition of pretreatment[1,2]. In the previous papers from this laboratory, it has been shown that the NiO-$TiO_2$ and NiO-$ZrO_2$ modified with sulfate ion is very active for ethylene dimerization even at room temperature[3-6]. High catalytic activities in the reactions were attributed to the enhanced acidic properties of the modified catalysts, which originated from the inductive effect of S=O bonds of the complex formed by the interaction of oxides with sulfate ion.

In this communication, we report the correlation between catalytic activity and acid strength of $TiO_2$ modified with various acids, $H_2SO_4$, $H_3PO_4$, $H_3BO_3$, and $H_2SeO_4$. For this purpose, the isomerization of 1-butene which is known to be catalyzed by acid catalysts[7-9] was chosen as test reaction.

The catalysts were prepared as follows. The precipitate of $Ti(OH)_2$ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of titanium tetrachloride and hydrochloric acid at room temperature with stirring until the pH of mother liquor reached about 7. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected, and was dried at room temperature. The dried precipitate was powdered below 100 mesh, and then the modification with acids was performed by pouring each 30 m*l* of 1N $H_2SO_4$, $H_3PO_4$, $H_3BO_3$, and $H_2SeO_4$ into 2 g of the powdered sample on a filter paper, respectively, followed by drying in air. The dry solid powder was used as catalyst after decomposing at different evacuation temperature for 1.5 hr. The catalysts modified with $H_2SO_4$, $H_3PO_4$, $H_3BO_3$, and $H_2SeO_4$ are referred as $TiO_2/SO_4^{2-}$, $TiO_2/PO_4^{3-}$, $TiO_2/BO_3^{3-}$, and $TiO_2/SeO_4^{2-}$, respectively.

The isomerization of 1-butene was carried out at 20°C by