

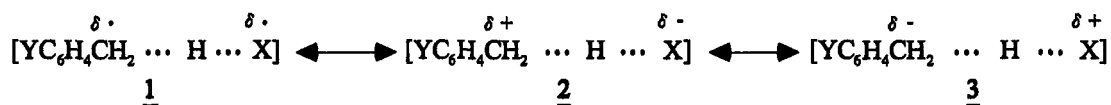
## Thornton rule for homolytic reactions

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**Abstract:** Numerous free radical reactions involve polar transition state (TS), which can be responsible for the excellent Hammett  $\rho^+ - \sigma^+$  correlations where the value of  $\rho^+$  is negative. The structure of polar TS can not be the resonance hybrid of the reactant and product of the radical reaction (the intermediate configuration). The deviation of the TS from the intermediate configuration (polarization of the TS) can be derived from the perpendicular effect (Thornton rule). The polar TS may accordingly invite nonlinear relations between the rates and the equilibria and the reactivities are controlled by the entropies. The perpendicular effects may invalidate Leffler-Hammond postulate and reactivity/selectivity principle.

The effects of the substituents (Y) on the rates of radical reactions in solutions have been a subject of interest for almost half a century (1, 2). When the homolytic cleavages take place at position  $\beta$  to a phenyl ring, i.e.  $\text{YC}_6\text{H}_4\text{CH}_2 + \text{X}\cdot \longrightarrow \text{YC}_6\text{H}_4\text{CH}_2\cdot + \text{HX}$ , the reactivities may be possibly accommodated with transition-state (TS) structures shown below.



The Hammett correlations of the radical reactions (3-11) show  $\rho^+ < 0$ , which indicates the major contribution of 2 to the rates. The structure 1 could be the resonance hybrid of the reactant,  $[\text{YC}_6\text{H}_4\text{CH}_2 \text{X}\cdot]$  and product,  $[\text{YC}_6\text{H}_4\text{CH}_2\cdot \text{HX}]$ . 2 apparently derivates from 1. When a TS assumes the intermediate configuration like 1, the substituent effects on the free energy of activation ( $\Delta G^\ddagger$ ) (kinetic substituent effects) and on the free energy of reaction ( $\Delta G^0$ ) (thermodynamic substituent effects) are linearly related with each other for a linear free energy relationship (12). When the subscripts Y and H signify the substituents on the phenyl ring, the linearity should also hold for the differentials that is  $\Delta \Delta G_{\text{Y-H}}^\ddagger = \alpha \Delta \Delta G_{\text{Y-H}}^0$  where  $\Delta G_{\text{Y}}^\ddagger - \Delta G_{\text{H}}^\ddagger = \Delta \Delta G_{\text{Y-H}}^\ddagger$  and  $\Delta G_{\text{Y}}^0 - \Delta G_{\text{H}}^0 = \Delta \Delta G_{\text{Y-H}}^0$ . Evans-Polanyi equation (13) is a simpler form of linear free energy relation. The parallelism between the rates and equilibria may well entertain Leffler-Hammond postulate (LHP) (12,14) and reactivity/selectivity principle (RSP) (15).

The breakdowns (16) of LHP and RSP were however recognized for many heterolytic reactions. Thornton (17) noted for the first time that the perturbations of potential energies of the TS by the substituents could take place in a perpendicular manner against the "normal" reaction coordinate (Thornton rule). The perpendicular effects could successfully rationalize the reactivities of various polar reactions (18-20), where the TS deviate from the aforementioned intermediate configuration. The polar TS such as 2 for the radical reactions (3-11) could be similarly considered to be the outcome of Thornton rule. The deviations due to the polar TS could thereby give rise to nonlinear differential substituent effects on the rates and equilibria with  $\Delta \Delta G_{\text{Y-H}}^\ddagger \neq \alpha \Delta \Delta G_{\text{Y-H}}^0$  (dual substituent effects).

### Breakdowns of LHP for the Radical Reactions

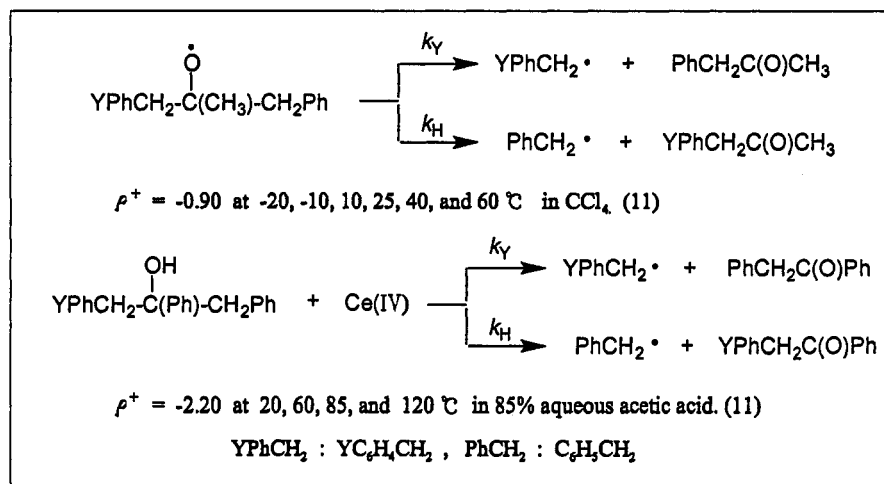
Various hydrogen abstractions and homolytic fragmentations traverse polar TS and exhibit excellent  $\rho^+ - \sigma^+$  correlations (Tables 1 and 2) (3-11). The ionizations (21) of cumyl chlorides also involve polar TS ( $\rho^+ = -4.45$ ), whose structures could be taken as the resonance hybrid of the cumyl chlorides and corresponding ion pairs. The rates of the ionizations should be thus related with the equilibrium constants of the ionizations.

Although the radical reactions (3-11) proceed through similar polar TS, the polarizations are the processes limited to the TS only and absent in the thermodynamic entities. In case of the ionizations of cumyl chlorides, the polarity of C-Cl bond gradually increases to finally produce the ion pairs. The polarization could be accordingly the synonym of the perpendicular effect. The homolytic cleavages (3-11) involving polar TS may thereby experience dual substituent effects to disobey LHP (12,14). The dualism may be also understood with Marcus theory [ $\Delta G^\ddagger = \Delta G_0^\ddagger + \Delta G^0/2 + (\Delta G^0)^2/16\Delta G_0^\ddagger$ ] (23). Compared to sigma dot ( $\sigma^\cdot$ ) (24), sigma plus ( $\sigma^+$ ) (21) varies remarkably to cause correspondingly notable variations of the intrinsic barrier ( $\Delta G_{0Y}^\ddagger$ ) for the polar TS. Since the intrinsic barriers ( $\Delta G_{0Y}^\ddagger$ ) are not constant with a series of the radical reactions (3-11), the corresponding  $\Delta G_Y^\ddagger$  could be determined by both  $\Delta G_{0Y}^\ddagger$  and  $\Delta G_Y^0$  to prohibit linear reaction between  $\Delta G_Y^\ddagger$  and  $\Delta G_Y^0$ .

TABLE 1. The hydrogen abstractions and Hammett correlations

R-H + X $\cdot$ $\longrightarrow$ R $\cdot$ + HX	Temp.( $^\circ$ C)	$\rho^+$	Reference
YC $_6$ H $_4$ CHO + (CH $_3$ ) $_3$ CO $\cdot$ $\longrightarrow$ YC $_6$ H $_4$ C $\dot{O}$ + (CH $_3$ ) $_3$ COH	130	-0.32	3
YC $_6$ H $_4$ CH=NC $_6$ H $_5$ + (CH $_3$ ) $_3$ CO $\cdot$ $\longrightarrow$ YC $_6$ H $_4$ C $\dot{C}$ =NC $_6$ H $_5$ + (CH $_3$ ) $_3$ COH	130	-0.98	4
C $_6$ H $_5$ CH=NC $_6$ H $_4$ Y + (CH $_3$ ) $_3$ CO $\cdot$ $\longrightarrow$ C $_6$ H $_5$ C $\dot{C}$ =NC $_6$ H $_4$ Y + (CH $_3$ ) $_3$ COH	130	-0.72	4
YC $_6$ H $_4$ SH + C $_6$ H $_5$ CO $_2$ $\cdot$ $\longrightarrow$ YC $_6$ H $_4$ S $\cdot$ + C $_6$ H $_5$ CO $_2$ H	100	-1.19	6
YC $_6$ H $_4$ OH + (CH $_3$ ) $_3$ CO $\cdot$ $\longrightarrow$ YC $_6$ H $_4$ O $\cdot$ + (CH $_3$ ) $_3$ COH	130	-1.46	10
YC $_6$ H $_4$ SH + (CH $_3$ ) $_3$ CO $\cdot$ $\longrightarrow$ YC $_6$ H $_4$ S $\cdot$ + (CH $_3$ ) $_3$ COH	130	-0.30	10
YC $_6$ H $_4$ CH $_3$ + Br $\cdot$ $\longrightarrow$ YC $_6$ H $_4$ CH $_2$ $\cdot$ + HBr	10	-1.17	5
	40	-1.26	5
	60	-1.33	5
	80	-1.41	5

TABLE 2. Homolytic fragmentations and Hammett correlations.



### Entropies of Activation as the Measures of the Bond Ruptures

The temperature studies of the hydrogen abstractions (5) and the  $\beta$ -scissions (9,11) disclose the critical role of the entropies for the rates. One can then envision the following changes of the entropies taking place during the activations. The vibrations of the C-H(C) bonds undergoing cleavages should be replaced by translational modes (a keynote of absolute rate theory) (25). The cleavages also erase the free rotations of the C-H(C) bonds. The conjugations of the benzylic carbocationic center with the adjacent phenyl ring could entail the hindered rotations. The translational mode implicates three dimensions and the rotations and vibrations are of two and one dimensions, respectively. The translational entropies enjoyed by the polar TS of the reactions (5,9,11) could thereby far exceed the decrease of the entropies caused by the disappearances of the vibrations and rotations, and the hindered rotations.

The electron-donating substituents (Y) then stabilize the fractional cationic center to augment the extent of the C-H(C) bond breakages and vice versa. The degrees of the cleavages of the C-H(C) (5,9,11) with different substituents (Y) could be thus reflected on the magnitudes of the entropies of activation ( $\Delta S_Y^\ddagger$ ) mostly derived from the translational entropies. The differential substituent effects on the entropies of activation can be defined as  $\Delta \Delta S_{Y-H}^\ddagger = \Delta S_Y^\ddagger - \Delta S_H^\ddagger$  where Y and H are the substituents on the phenyl ring with the hydrogen abstractions (5) and homolytic fragmentations (9,11). The values of  $\Delta \Delta S_{Y-H}^\ddagger$  for the reactions (5,9,11) have been computed. The plots of  $\Delta \Delta S_{Y-H}^\ddagger$  vs.  $\sigma^+$  yield straight lines with negative slopes (Fig. 1) which is compatible with the foregoing statements regarding the differential substituents effects on the degree of the bond breakages. Figure 1 may be therefore pronouncing the entropy control of reactivities.

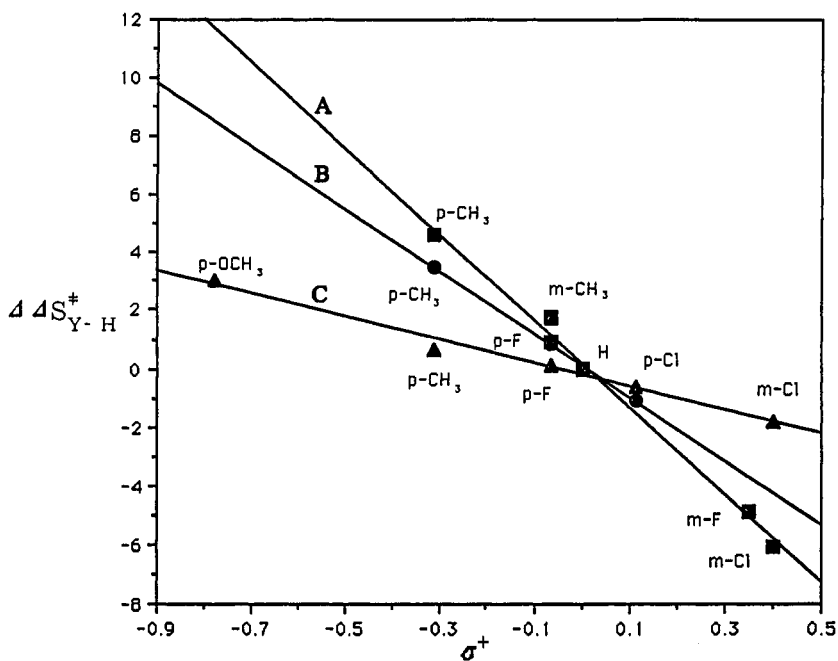


Fig. 1. Plot of  $\Delta \Delta S_{Y-H}^\ddagger$  vs.  $\sigma^+$

- A : ■ for Photobrominations of toluenes by N-bromsuccinimide. (5)  
 B : ● for Homolytic fragmentations of benzyl methyl substituted-benzyl carbinolxy radicals. (9, 11)  
 C : ▲ for Oxidative cleavages of 1-aryl-2,3-diphenylpropan-2-ols by Ce(IV). (11)

### Entropic Dominance Responsible for Non-RSP Behavior

The selectivity  $S$  of a species in its reaction with the competing reagents harboring substituents  $Y$  and  $H$  could be defined by  $S = \ln k_Y/k_H = -(\Delta G_Y^\ddagger - \Delta G_H^\ddagger)/RT = -\Delta\Delta G_{Y-H}^\ddagger/RT$ , with  $k$  and  $\Delta G^\ddagger$  being the corresponding rate constant and free energy of activation, respectively.  $S = -\Delta\Delta G_{Y-H}^\ddagger/RT$  can be subdivided into two parts:  $-\Delta\Delta G_{Y-H}^\ddagger/RT = \Delta\Delta S_{Y-H}^\ddagger/R - \Delta\Delta H_{Y-H}^\ddagger/RT$ . Since  $S = \ln k_Y/k_H = \rho^+\sigma^+$  and  $\sigma^+$  is a substituent constant,  $\rho^+ = S/\sigma^+$  can be also counted as an selectivity index. The hydrogen abstraction from toluenes by bromine atom shows that  $\rho^+$  become negatively larger with increasing temperature i.e.  $\rho^+ = -1.17$  (10 °C),  $-1.26$  (40 °C),  $-1.33$  (60 °C), and  $-1.41$  (80 °C). (Table 1). The trends of  $\rho^+$  with temperature apparently violate RSP because selectivities increase with higher temperatures. The calculations of the differential activation parameters indicate that the values of  $\Delta\Delta H_{Y-H}^\ddagger$  are much smaller than that of  $\Delta\Delta S_{Y-H}^\ddagger$  (refer to Table 2 of 5). Since isokinetic relations (26) hold for this abstractions,  $\Delta\Delta H_{Y-H}^\ddagger$  and  $\Delta\Delta S_{Y-H}^\ddagger$  must retain the same sign whether positive or negative. Increase of temperature should therefore boost the selectivities ( $S = \Delta\Delta S_{Y-H}^\ddagger/R - \Delta\Delta H_{Y-H}^\ddagger/RT$ ) to defy RSP. The two fragmentation reactions (9,11) show constant  $\rho^+$  values, respectively, irrespective of the temperature change, i.e.  $\rho^+ = -0.9$  at  $-20$  °C  $\sim$   $60$  °C and  $\rho^+ = -2.20$  at  $20$  °C  $\sim$   $120$  °C (Table 2). The selectivity index  $\rho^+$  is hardly influenced by the temperature. The computations of the differential parameters ( $\Delta\Delta H_{Y-H}^\ddagger$  and  $\Delta\Delta S_{Y-H}^\ddagger$ ) reveal that the magnitudes of  $\Delta\Delta H_{Y-H}^\ddagger$  are close to zero while those of  $\Delta\Delta S_{Y-H}^\ddagger$  maintain sizable figures. (refer to Tables 2 and 5 of 11) The selectivities ( $S$ ) must be therefore determined by  $\Delta\Delta S^\ddagger/R$  term only which does not contain temperature factor.

### Conclusion

The hydrogen abstractions have been normally depicted as a combination of the two anharmonic vibrations on two-dimensional reaction profile. According to Thornton rule, the paths of the potential energies of the radical reactions involving polar TS should be accommodated with three-dimensional system where the polar TS is significantly displaced from the "conventional" reaction coordinate. The polar TS may be derived from either the perpendicular effects or the variable intrinsic barriers, which may provoke the entropic dominance for the rates.

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### References

1. C. Walling, *Free Radicals in Solution*, Wiley, New York, Chapter 8 (1957).
2. G. A. Russell, *Free Radicals*, J. K. Kochi, Ed., Wiley, New York, Vol. 1, Chapter 7 (1973).
3. S. S. Kim, S. C. Sohn. *Tetrahedron Lett.* **23**, 3703 (1982).
4. S. S. Kim, H. M. Koo and S. Y. Choi. *Tetrahedron Lett.* **26**, 891 (1985).

5. S. S. Kim, S. Y. Choi and C. H. Kang. *J. Am. Chem. Soc.* **107**, 4234 (1985).
6. S. S. Kim, J. S. Seo and M. H. Yoon. *J. Org. Chem.* **52**, 3691 (1987).
7. S. S. Kim, C. S. Lee, C. C. Kim and H. J. Kim. *J. Phys. Org. Chem.* **3**, 803 (1990).
8. S. S. Kim, K. S. Lee, S. B. Hwang and H. J. Kim. *Tetrahedron Lett.* **31**, 3575 (1990).
9. S. S. Kim, C. J. Kim, S. J. Youn, H. S. Ra and J. C. Lee. *Tetrahedron Lett.* **32**, 4725 (1991).
10. S. S. Kim, S. Y. Kim, S. S. Ryou, C. S. Lee and K. H. Yoo. *J. Org. Chem.* **58**, 192 (1993).
11. S. S. Kim, H. R. Kim, H. B. Kim, S. J. Youn and C. J. Kim. *J. Am. Chem. Soc.* **116**, 2754 (1994).
12. J. E. Leffler. *Science* **117**, 340 (1953).
13. M. G. Evans and M. Polanyi. *Trans. Faraday Soc.* **34**, 11 (1938).
14. G. S. Hammond. *J. Am. Chem. Soc.* **77**, 334 (1955).
15. J. E. Leffler and E. Grunwald. *Rates and Equilibria of Organic Reactions*, Wiley, New York (1963)
16. (a) B. Giese. *Angew. Chem. Int. Ed. Engl.* **16**, 125 (1977).  
(b) A. Pross. *Adv. Phys. Org. Chem.* **14**, 69 (1977).  
(c) C. D. Johnson. *Chem. Rev.* **75**, 755 (1975).  
(d) W. P. Jencks. *Chem. Rev.* **85**, 511 (1985).
17. E. R. Thornton. *J. Am. Chem. Soc.* **89**, 2915 (1967).
18. M. O'Ferrall. *J. Chem. Soc. B.* 274 (1970).
19. W. P. Jencks. *Chem. Rev.* **72**, 705 (1972).
20. W. J. Albery and M. M. Kreevoy. *Adv. Phys. Org. Chem.* **16**, 87 (1978).
21. H. C. Brown and Y. Okamoto. *J. Am. Chem. Soc.* **80**, 4979 (1958).
22. G. A. Russell. *J. Org. Chem.* **23**, 1407 (1958).
23. R. A. Marcus. *J. Phys. Chem.* **72**, 891 (1968).
24. J. M. Dust and D. R. Arnold. *J. Am. Chem. Soc.* **105**, 1221 and 6531 (1983).
25. H. Eyring. *J. Chem. Phys.* **3**, 107 (1935).
26. J. E. Leffler. *J. Org. Chem.* **20**, 1202 (1955).