g, 20 mmol) with activated zinc (1.3 g, 20 mmol) in 10 m*l* of acetic anhydride.[13]

In conclusion, trifluoromethyl group can be easily introduced into thebaine system *via* addition or Diels-Alder reaction which depends on the solvent, and plays an important role for the formation of retro Diels-Alder adduct.

Acknowledgement. We thank the Ministry of Science and Technology for financial support, and Dr. S. K. Choi for recording the ^{19}F NMR spectra.

References

1. K. W. Bentley, "The Alkaloids", R. H. F. Manske, Ed., Vol. 13, Chapter 1, Academic Press, New York (1971).
2. (a) K. W. Bentley and D. G. Hardy, *J. Am. Chem. Soc.*, **89**, 3267 (1967); (b) K. W. Bentley, D. G. Hardy and B. Meek, *ibid.*, **89**, 3273 (1967); (c) K. W. Bentley and D. G. Hardy, *ibid.*, **89**, 3281 (1967); (d) K. W. Bentley, D. G. Hardy and B. Meek, *ibid.*, **89**, 3293 (1967); (e) K. W. Bentley, D. G. Hardy, C. F. Howell, W. Fulmor, J. E. Lancaster, J. J. Brown, G. O. Morton and R. A. Hardy, Jr., *ibid.*, **89**, 3303 (1967); (f) K. W. Bentley, D. G. Hardy, H. P. Crocker, D. I. Haddlesey and P. A. Mayor, *ibid.*, **89**, 3312 (1967).
3. J. W. Lewis, M. J. Readhead, I. A. Selby, A. C. B. Smith and C. A. Young, *J. Chem. Soc.* (C), 1158 (1971).
4. (a) R. Giger, R. Rubinstein and D. Ginsburg, *Tetrahedron*, **29**, 2387 (1973); (b) R. Rubinstein, F. Haviv and D. Ginsburg, *ibid.*, **30**, 1201 (1974).
5. I. Fujii, K. Ryu, K. Hayakawa and K. Kanematsu, *J. Chem. Soc. Chem. Commun.*, 844 (1984).
6. J. J. Kopcho and J. C. Schaeffer, *J. Org. Chem.*, **51**, 1620 (1986).
7. (a) C. W. Hutchins, G. K. Cooper, S. Purro and H. Rapoport, *J. Med. Chem.*, **24**, 773 (1981); (b) L. L. Knipmeyer and H. Rapoport, *J. Med. Chem.*, **28**, 461 (1985); (c) P. J. Maurer and H. Rapoport, *J. Med. Chem.*, **30**, 2016 (1987).
8. H. Rapoport and P. Sheldrick, *J. Am. Chem. Soc.*, **85**, 1636 (1963).
9. (a) K. Hayakawa, S. Motohiro, I. Fujii and K. Kanematsu, *J. Am. Chem. Soc.*, **103**, 4605 (1981); (b) K. Hayakawa, I. Fujii and K. Kanematsu, *J. Org. Chem.*, **48**, 166 (1983).
10. (a) A. Singh, S. Archer, K. Hoogsteen and J. Hirshfield, *J. Org. Chem.*, **47**, 754 (1982); (b) A. Singh, S. Archer, K. Hoogsteen and J. Hirshfield, *J. Org. Chem.*, **48**, 173 (1983).
11. R. Filler and Y. Kobayashi, "Biomedicinal Aspects of Fluorine Chemistry", Kodansha, Tokyo (1982).
12. W. P. Norris and W. G. Finnegan, *J. Org. Chem.*, **31**, 3292 (1966).
13. A. L. Henne and W. G. Finnegan, *J. Am. Chem. Soc.*, **71**, 298 (1949).
14. F. E. Herkes and H. E. Simmons, *J. Org. Chem.*, **38**, 2845 (1973).
15. M. Green, N. Mayne and F. G. A. Stone, *Chem. Commun.*, 785 (1966).
16. D. M. Wiemers, Ph. D. Thesis, University of Iowa, 1987.
17. R. M. Silverstein, G. C. Bassler and T. C. Morrill, "Spectrometric Identification of Organic Compounds", John Wiley & Sons, New York (1981).

Resonance Bond-Contraction Demonstrated by Cross-Interaction Constants

Ikchoon Lee

Department of Chemistry, Inha University, Inchon 402-751

Received January 24, 1990

The cross interaction constants ρ_{ij} in eq. (1) have been shown to be a very versatile tool for characterizing transition state (TS) structures, especially in S_N2 reactions.[1] We present here a novel application of the cross-interaction constants to demonstration of resonance contraction of a bond in the S_N2 TS.

$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \tag{1}$$

The sign of ρ_{ij} provides criteria for predicting substituent effects on the TS variation in S_N2 reactions.[1c,e] For example, if ρ_{XZ} is negative (Scheme 1), a stronger nucleophile ($X = p$-OCH$_3$) as well as a stronger nucleofuge ($Z = p$-NO$_2$) leads to a later TS so that eqs. (2) apply, whereas if ρ_{XZ} is positive the

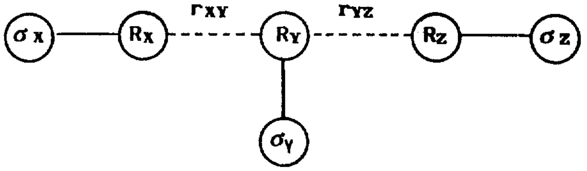
$$\left.\begin{array}{ll} \Delta r_{YZ} = a\sigma_X & a<0 \\ \Delta r_{XY} = a'\sigma_Z & a'<0 \end{array}\right\} \tag{2}$$

opposite effects are predicted so that the signs of a and a′ in Eqs. (2) reverse to positive.[1c,e,2] On the other hand, the distance r_{ij} in Scheme 1 is shown to be a logarithmic inverse function of the magnitude of ρ_{ij}[2,3] so that another set of relations are obtained with positive constants, b and b', for

$$\left.\begin{array}{ll} \Delta\log|\rho_{YZ}| = b\sigma_X & b>0 \\ \Delta\log|\rho_{XY}| = b'\sigma_Z & b'>0 \end{array}\right\} \tag{3}$$

$\rho_{XZ}<0$, which reverse to negative ($b, b'<0$) for $\rho_{XZ}>0$.

In our previous works, it has been shown that the S_N2 reaction of anilines with benzyl benzenesulfonates, reaction (I)[4], belongs to the former category *i.e.*, $\rho_{XZ}<0$ with negative a (a') and positive b (b'), whereas that with phenacyl benzenesulfonates, reaction (II),[1c] belongs to the latter type, *i.e.*, $\rho_{XZ}>0$ with positive a (a') and negative b (b').

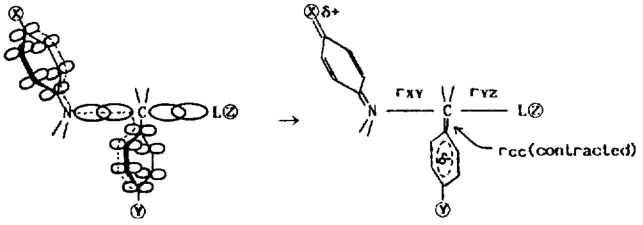


$i, j = X$, Y or Z in eq. (1); $r_{XZ} + r_{YZ}$. σ_i and R_i are substituents and reaction centers in the nucleophile (X), substrate (Y) and leaving group (Z).

Scheme 1

Table 1. The ρ_{YZ} Values for Reaction I and II.

X =	p-OCH$_3$	p-CH$_3$	H	p-Cl	m-NO$_2$
Reaction I	0.35	0.20	0.11	0.13	0.14
Reaction II	-0.63	-0.65	-0.66	-0.67	—



Two benzene rings are perpendicular to the paper plane.

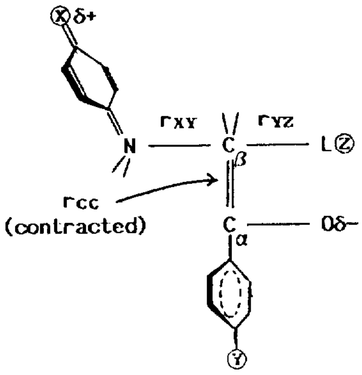
Scheme 2

$$2XC_6H_4NH_2+YC_6H_4CH_2OSO_2C_6H_4Z$$
$$\rightarrow YC_6H_4CH_2NHC_6H_4X+XC_6H_4NH_3^++{}^-OSO_2C_6H_4Z, \qquad (I)$$

$$2XC_6H_4NH_2+YC_6H_4COCH_2OSO_2C_6H_4Z$$
$$\rightarrow YC_6H_4COCH_2NHC_6H_4X+XC_6H_4NH_3^++{}^-OSO_2C_6H_4Z, \qquad (II)$$

Thus r_{YZ} should decrease, and hence $|\rho_{YZ}|$ should increase, as the nucleophile becomes weaker, *i.e.*, $\Delta r_{YZ}<0$ and $\Delta \log |\rho_{YZ}|>0$ for $\sigma_X>0$, in reaction (I). The $|\rho_{YZ}|$ value was indeed found to increase as the nucleophile gets weaker from X = H to X = *m*-NO$_2$, but $|\rho_{YZ}|$ is seen to increase as the nucleophilicity increases from X = H to X = *p*-OCH$_3$ *i.e.*, $\Delta \log |\rho_{YZ}|>0$ for $\sigma_X<0$ and $b>0$, in contradiction to the trend expected from eqs. (3) (Table 1). This inconsistency for the electron-donating substituents in the nucleophile (X = *p*-CH$_3$ and *p*-OCH$_3$) results from a "benzylic effect",[5] not from a decrease in r_{YZ} (Scheme 2). The substrate ring (with Y) attracts electrons from an electron-donating group, X, through π-overlaps involving the benzylic *p*-orbital, and as a result of this delocalization the bond between C_α and the ipso-carbon atom of the substrate is contracted ($\Delta r_{CC}<0$). This means that the distance between substituents Y and Z can be reduced despite the increased bond cleavage due to a greater nucleophilicity ($\Delta r_{YZ}>0$ for $\sigma<0$ and $a<0$ in eqs. 2) so that $|\rho_{YZ}|$ increases *i.e.*, $\Delta r_{CC}<0$ and $\Delta r_{YZ}>0$ but $(\Delta r_{CC}+\Delta r_{YZ})<0$ since $|\Delta r_{CC}|>|\Delta r_{YZ}|$ and hence $\Delta|\rho_{YZ}|>0$. The delocalization of π-electrons on X is possible since the π-orbital in the aniline nucleophile can overlap with the benzylic *p*-orbital at an angle of ca.30° which will provide more than 85% (cos30 = 0.866) π-overlap.[5a] This benzylic effect is greater with a stronger nucleophile ($\sigma_X<0$), and hence r_{CC} in Scheme 2 becomes shorter ($\Delta r_{CC}<0$), since a stronger nucleophile leads to a tighter TS,[6] *i.e.*, $\Delta r_{XY}<0$, and hence the overlap of the two π-clouds in the two rings becomes more efficient. In fact, use of the dual substituent parameter equations of the type in eq. (4) has shown a remarkably greater resonance-to-polar (reaction constant) ratio,

$$\log(k_Y/k_0)=\rho_{pol}\sigma_{pol}+\rho_R\sigma_R \qquad (4)$$



Two rings are perpendicular to the paper plane.

Scheme 3

ρ_R/ρ_{pol}, for such an electron-donating substituent (X = *p*-CH$_3$ or *p*-OCH$_3$) in the nucleophile[7] reflecting a strong resonance contribution to the substituent effects in the substrate (ρ_Y).

On the other hand, we note in Table 1 that for reaction (II), $|\rho_{YZ}|$ increases as the nucleophile becomes weaker ($\sigma_X>0$) suggesting a decrease in the distance between the substituents Y and Z. This appears to contradict with the trend expected from a reaction with $\rho_{XZ}>0$, for which bond cleavage should increase and hence $|\rho_{XZ}|$ should decrease with a weaker nucleophile since $\Delta r_{YZ}>0$ for $a>0$ and $\sigma_X>0$ in eqs. (2) for this type of reaction. This apparent inconsistency can be rationalized with the "resonance shunt" effect of the α-carbonyl group.[1c] This effect is similar to the benzylic effect in that the overlap of π-orbital in the nucleophile and the *p*-orbital of the reaction center (C_β) provides delocalization of electron density on the substituent X into the carbonyl oxygen in the TS resulting in a bond contraction, $\Delta r_{cc}<0$ (Scheme 3). Conjugation of X with the substrate ring is partially prevented by this "shunt" effect of the carbonyl group. However, the overlap of the reaction center (C_β) *p*-orbital and the π-orbital of the carbonyl carbon (C_α) is considerably more efficient, in addition to a strong electronegative electron-attracting effect of the carbonyl oxygen.

The resonance contraction of r_{CC} ($\Delta r_{CC}<0$ in Scheme 3) lead to an increase in $|\rho_{YZ}|$, which is not due to a decrease in r_{YZ}. In fact, bond cleavage should increase with a weaker nucleophile, *i.e.*, $\Delta r_{YZ}>0$ for $\sigma_X>0$ and $a>0$ for this type with $\rho_{XZ}>0$ in eqs. (2), so that an increase in $|\rho_{YZ}|$ indicates a net decrease in the distance between Y and Z, *i.e.*, $(\Delta r_{CC}+\Delta r_{YZ})<0$, since $|\Delta r_{CC}|>|\Delta r_{YZ}|$. This work therefore demonstrates that the resonance contraction of r_{CC} is somewhat greater than the bond length changes involved in the TS due to substituent variation (Δr_{XY} or Δr_{YZ}), so that Δr_{CC} ($= r_{C-C}-r_{C-C} = 1.51-1.39 \cong 0.12$ Å)[13] can cause an observable change in the magnitude of ρ_{YZ}, since $\Delta r_{CC}<0$ and $\Delta r_{YZ}>0$ but $(\Delta r_{CC}+\Delta r_{YZ})<0$; this is reasonable since total bond length changes of 20∼30%[14] (1.51 × (0.2∼0.3) = 0.30∼0.45 Å) in the TS are normally thought to occur, and hence Δr_{XY} or Δr_{YZ} due to substituent changes (10% of the total changes)[15] should be even smaller than this total bond length changes.

Furthermore the resonance contraction due to the "shunt" seems to be somewhat smaller compared to that due to the benzylic effect, since the $\Delta|\rho_{YZ}|$ values for changes in X from H to p-OCH_3 were 0.03 and 0.24 for the former (reaction (II)) and for the latter (reaction (I)) respectively.

This type of resonance contraction ($\Delta r_{CC}<0$) can not be experimentally measured nor can be demonstrated with other selectivity parameters such as simple Hammett constants, ρ_i, or Brönsted constants, β_i; the demonstration is only possible, at the present, with an observed increase in the magnitude of cross-interaction constants, ρ_{YZ}.

Acknowledgement. We thank the Korea Science and Engineering Foundation and the Ministry of Education for support of this work.

References

1. (a) I. Lee and S. C. Sohn, *J. Chem. Soc., Chem. Commun.*, 1055 (1986); (b) I. Lee, H. K. Kang, and H. W. Lee, *J. Am. Chem. Soc.*, **109**, 7472 (1987); (c) I. Lee, C. S. Shim, S. Y. Chung, H. Y. Kim, and H. W. Lee, *J. Chem. Soc., Perkin Trans. 2*, 1919 (1988); (d) I. Lee, C. S. Shim, S. Y. Chung, and H. W. Lee, *J. Chem. Soc., Perkin Trans 2*, 975 (1988); (e) I. Lee, Y. H. Choi, H. W. Lee, and B. C. Lee, *J. Chem. Soc., Perkin Trans. 2*, 1537 (1988); (f) I. Lee, H. Y. Kim, H. K. Kang, and H. W. Lee, *J. Org. Chem.*, **53**, 2678 (1988); (g) I. Lee, C. S. Shim, and H. W. Lee, *J. Chem. Soc., Perkin Trans. 2*, 1205 (1989); (h) I. Lee, H. Y. Kim, H. W. Lee, and I. C. Kim, *J. Phys. Org. Chem.*, **2**, 35 (1989); (i) I. Lee, Y. H. Choi, K. W. Rhyu, and C. S. Shim, *J. Chem. Soc., Perkin Trans. 2*, 1881 (1989).
2. I. Lee, *J. Chem. Soc., Perkin Trans. 2*, 943 (1989).
3. I. Lee, *Bull. Korean Chem. Soc.*, **9**, 179 (1988).
4. (a) I. Lee, H. W. Lee, S. C. Sohn, and C. S. Kim, *Tetrahedron*, **41**, 2635 (1985); (b) I. Lee, S. C. Sohn, C. H. Kang, and Y. J. Oh, *J. Chem. Soc., Perkin Trans. 2*, 1631 (1986); (c) I. Lee, S. C. Sohn, Y. J. Oh, and B. C. Lee, *Tetrahedron*, **42**, 4713 (1986).
5. (a) J. F. King and G. T. Y. Tsang, *J. Chem. Soc., Chem. Commun.*, 1131 (1979); (b) J. I. Lynas-Gray, and C. J. M. Sterling, *J. Chem. Soc., Chem. Commun.*, 483 (1984); (c) D. Kost, and K. Aviram, *J. Am. Chem. Soc.*, **108**, 2006 (1986); (d) T. L. Amyes and W. P. Jencks, *J. Am. Chem. Soc.*, **111**, 7900 (1989).
6. Our recent works on the inverse secondary kinetic isotope effect ($k_H/k_D<1.0$) involving deuterated aniline nucleophiles in reaction 4 indicated that k_H/k_D decreases, *i.e.*, the TS is tighter ($\Delta r_{XY}<0$) with a more electron donating substituent in the nucleophile ($\sigma_X<0$). I. Lee, H. J. Koh, B.-S. Lee, and H. W. Lee, *J. Chem. Soc., Chem. Commun.*, 335 (1990).
7. I. Lee and S. C. Sohn, *Bull. Korean Chem. Soc.*, **7**, 323 (1986); all four types of dual substituent parameter equations (Yukawa-Tsuno-Jencks,[8] Taft,[9,10] Swain-Lupton[11] and Afanas'ev[12]) tested gave large ρ_R/ρ_I values for $X=p$-CH_3 and p-OCH_3 in eq. (4).
8. (a) P. R. Young and W. P. Jencks, *J. Am. Chem. Soc.*, **99**, 8238 (1977); (b) P. R. Young and W. P. Jencks, *J. Am. Chem. Soc.*, **101**, 3288 (1979).
9. (a) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959); (b) R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5352 (1959).
10. (a) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 1 (1973); (b) M. Charton, *Prog. Phys. Org. Chem.*, **13**, 119 (1981).
11. (a) C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, **90**, 4328 (1968); (b) C. Hansch, A. Leo, S. H. Unger, K. H. Kim, D. Nikaitani, and E. J. Lien, *J. Med. Chem.*, **16**, 1207 (1973).
12. I. B. Afanas'ev, *J. Chem. Soc., Perkin Trans. 2*, 1589 (1984).
13. L. E. Sutton, ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Spec. Pub. No. 18; The Chem. Soc.: London, 1965.
14. I. Lee, J. K. Cho, H. S. Kim, and K. S. Kim, *J. Phys. Chem.*, **94**, 5190 (1990).
15. I. Lee and C. H. Song, *Bull. Korean Chem. Soc.*, **7**, 186 (1986).

Reaction Mechanism for Acyl-Transfer Reactions of Aryl Acetates with Aryloxides

Dong-Sook Kwon, Gwang-Ju Lee, and Ik-Hwan Um*

Department of Chemistry, Ewha Womans University, Seoul 120-750

Received January 29, 1990

Although acyl-transfer reactions have been known significantly important in chemistry and biochemistry and numerous studies have been performed, the reaction has not been well understood.[1-3] It has frequently been proposed that acyl-transfer reactions of aryl or thioaryl acetates with various amines and thiolates proceed *via* stepwise mechanisms, *i.e.* formation and breakdown of tetrahedral intermediates in which the rate-determining step may vary depending on nucleofugalities of the attacking and leaving groups.[2] However, until quite recently one step concerted mechanisms have also been suggested for most acyl-transfer reactions.[3]

The arguments concerning with the reaction mechanisms are mainly based on studies of linear free energy relationship (LFER), and the discrepancy seems to originate mostly from difficulties in interpretations of the effect of polar substituents in the attacking and leaving groups on rate constants. The LFERs including Brønsted and Hammett type treatment have been most commonly used for mechanistic investigations.[4,5] For many decades and for most reactions still today, the most valuable information on the determination of transition state (TS) structure has been obtained from the study of LFER.[4-6]

Recently we have reported that medium compositions would exert a significant influence on the α-effect as well as on reaction rates for the acyl-transfer reactions of p-nitrophenyl acetate with oxygen centered nucleophiles.[7] Moreover, we have also observed unusual rate decreases upon addition of an aprotic solvent into the reaction medium. However, a plausible explanation for the results was not given