

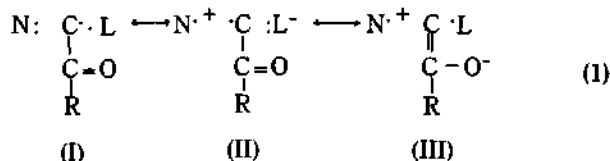
"Resonance Shunt" Phenomenon in Nucleophilic Substitution of α -Carbonyl Derivatives Demonstrated by the Cross Interaction Constants

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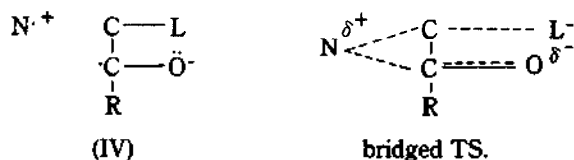
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The nucleophilic substitution reactions of α -carbonyl derivatives have attracted considerable attention of theoretical¹ as well as experimental² organic chemists due to many aspects of the reaction mechanism that remain controversial and not well understood. Recently McLennan and Pross³ applied the valence-bond configuration mixing (VBCM) model to explain the mechanism by which the rate-enhancing effect of the carbonyl group is transmitted to the reaction center.

As Dewar⁴ suggested, the α -CO group is shown to stabilize the transition state (TS) through resonance delocalization involving an enolate ion, (III) in eq (1). They argued that the three configurations, reactant (I), product (II) and the enolate form (III) of carbanion, suffice to express the TS structure



for the S_N2 reactions of α -carbonyl compounds. However, the carbanion configuration can also accommodate structure (IV), which would lead to bridging in the TS as Winstein⁵ suggested.

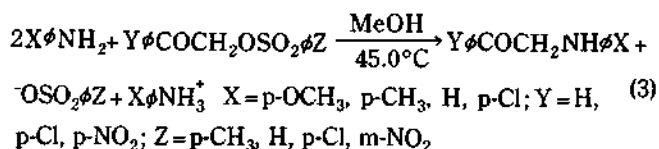


Recently, we have introduced mechanistic criteria based on the inverse distance dependence of cross interaction constant ρ_{ij} between substituents i and j , eq (2).⁶ The criteria have been

$$\log(k_{ij}/k_{HH}) = \rho_i \sigma_i + \rho_j \sigma_j + \rho_{ij} \sigma_i \sigma_j \quad (2)$$

successfully applied towards the rationalization of various mechanistic details involved in nucleophilic substitution^{6a}, identity reaction^{6b}, elimination^{6c} and retentive displacement.^{6d}

We report here the results of our determination of ρ_{ij} values and application to the elucidation of the TS structure for reaction (3).



Second order rate constants k_{ij} with substituents i and j in (3) (12-16 values) have been determined and were subjected to multiple linear regression analysis⁷ using eq (2), and cross interaction constants ρ_{ij} were determined. The results are

Table 1. Cross Interaction Constants, ρ_{ij} , for Reaction (3) at 45.0°C ($r \geq 0.998$)

	X = p-OCH ₃	p-CH ₃	H	p-Cl
ρ_Y	0.60	0.64	0.66	0.67
ρ_Z	1.14	1.17	1.23	1.30
ρ_{YZ}	-0.62	-0.65	-0.66	-0.67
$\rho_{XY} (Z = \text{H})$	0.12			
$\rho_{XZ} (Y = \text{H})$	0.32			

summarized in Table 1.

We note that the magnitude of ρ_{YZ} is relatively large compared with those for methanolysis ($\rho_{YZ} = -0.07$ at 45°C)⁸ and E1cB-like elimination reaction ($\rho_{YZ} = -0.57$ at 40°C)⁹ of an alkyl analogue, 2-phenylethyl benzenesulfonates $Y\phi\text{CH}_2\text{CH}_2\text{OSO}_2\phi\text{Z}$. This indicates that bond breaking has progressed very little in the TS of reaction (3). The size of ρ_{XZ} is also relatively large,¹⁰ implying again the small degree of bond cleavage.

Two anomalies are recognized in the size of ρ_{ij} values in Table 1: (i) The $|\rho_{XY}|$ is unusually small, and (ii) the $|\rho_{YZ}|$ increases in parallel with ρ_Y and ρ_Z values. The magnitude of ρ_{XY} values for other S_N2 reactions were found to range from 0.60 to 1.20,¹¹ and hence the ρ_{XY} values of 0.12 in Table 1 should be considered abnormally small. This anomalously low ρ_{XY} value can, however, be rationalized by taking into account a "shunt" or a "leak" provided by the α -CO group in the resonance between the reaction center, C_β , and the substituent Y, as in (III). This constitutes a counterpart of "resonance saturation" phenomena¹⁵ observed in the reactions with cationic reaction center in the TS. Since charge transfer from the nucleophile to the reaction center is greater than that from the reaction center to the leaving group, the reaction center is negatively charged in the TS as the positive ρ_Y values suggest in Table 1. Thus delocalization of negative charge into the α -CO group, (III), decreases the electron supply to the substituted (Y) benzene ring so that the interaction between substituents X and Y, and hence $|\rho_{XY}|$ decreases.

Although bond formation proceeds substantially, as the relatively large ρ_{XZ} value¹⁰ indicates, the interaction between X and Y is weakened markedly, not due to the large distance involved but due to a "shunt" or a "leak" in the resonance provided by the α -CO group. This interpretation is also supported by the second anomaly noted above: the parallel increase in the $|\rho_{YZ}|$ value with ρ_Y and ρ_Z . The size of ρ_Y and ρ_Z value in Table 1 indicates that charge transfer from the nucleophile to the reaction center (ρ_Y) as well as that from the reaction center to the leaving group (ρ_Z) increases with the more electron withdrawing substituent (EWS) in the nucleophile, e.g. $X = \text{p-Cl}$. The increase in the ρ_Z value within a series of reaction can be normally taken as the increase in bond cleavage; bond breaking increases with the more EWS in the nucleophile, which should result in a decrease, in con-

trast with an increase observed, in the $|\rho_{YZ}|$ values. This can be rationalized with the enhanced contribution of resonance "shunt" by the α -CO as the charge transfer increases, which has a shortening effect on the C_α - C_β bond length due to the double bond character in structure (III); the greater degree of charge transfer (the larger ρ_Y) will bring the greater contribution of resonance shunt, which in turn will result in a shorter C_α - C_β bond. The shorter C_α - C_β bond will naturally mean a larger $|\rho_{YZ}|$ value as observed; hence the parallel increase in the $|\rho_{YZ}|$ with ρ_Y and ρ_Z can be accommodated.

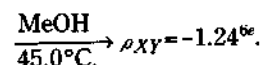
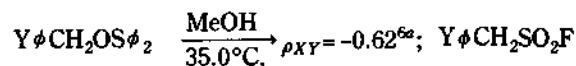
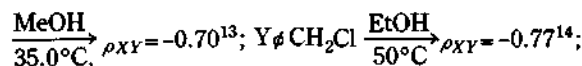
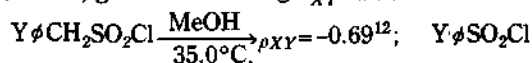
In structure (IV), there is an unpaired electron on C_α so that the substituent Y can interact with the C_β atom, which in turn means the interaction between X and Y; there will be no decrease in the interaction (and hence in ρ_{XY}) between X and Y. Thus our results clearly support involvement of structure III, but not (IV), in the TS of the nucleophilic substitution reaction of α -carbonyl compounds. We can conclude that the involvement of the bridged TS structure is a tenuous one in the light of our results of cross interaction constants.

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A Convenient Synthesis of (E)- β -Farnesene

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(E)- β -Farnesene(**1**), (6E)-7,11-dimethyl-3-methylene-1,6,10-dodecatriene (Fig. 1) was known as a constituent of various essential oils¹ and recently used for enhancing the aroma of perfumed materials, e.g. soaps, detergents, and magnolia fragrance². In 1972, W.S. Bowers identified (E)- β -farnesene as an alarm pheromone of several economically important species of aphids³. The damage to crops by aphids either by feeding or by transmitting virus disease can be prevented to some extent by insecticides, but aphids are

developing increased resistance, particularly to systemic organophosphates⁴. Also, such insecticides do not prevent damage to crops by non-persistent viruses, such as potato virus Y, since these are rapidly acquired and transmitted by aphids. The fast-acting pyrethroids may control infection with non-persistent viruses⁵ but are less effective with the more resistant biotypes *Myzus persicae*, so alternative novel approaches appear desirable. Of the chemicals that influence aphid behavior, the most active is the alarm pheromone⁶