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A MEASURE OF CHARGE TRANSFER (ρ) VERSUS A MEASURE OF BOND TIGHTNESS (ρ_{ij}) IN THE TRANSITION STATE.

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Abstract: An example has been presented in which ρ is only a measure of charge transfer whereas ρ_{ij} serves as a measure of bond tightness in the transition state.

The size of the Hammett reaction constant ρ is commonly believed to give an indication of the extent of charge development at the atom of the reaction site which is directly involved in the bond making and breaking processes at the transition state (TS)[1]. However it has been suggested that ρ values can not be used as a measure of TS structure, since the efficiency of charge transmission for different reaction series may differ.[1,2]

In this work we wish to present such an example showing the failure of ρ values as a direct measure of the degree of bond making in the TS; we propose instead the use of the absolute value of the cross interaction constants ρ_{ij} as a quantitative measure of bond tightness in the TS.[3]

In a previous report[3] we have shown that the magnitude of cross interaction constant ρ_{XY} between substituents X and Y (eq 1) is inversely proportional to the distance between

$$\log (k_{XY} / k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \qquad (1)$$

X and Y in the TS; thus in the nucleophilic substitution reaction between a nucleophile with substituent X and a substrate with Y, the degree of bond making will be greater the larger the $|\rho_{XY}|$, since the larger $|\rho_{XY}|$ is an indication of the closer distance between the nucleophile with X and the substrate with Y.[3] This will be true irrespective of the size of the individual ρ_X and / or ρ_Y values in eq (1).

We have recently conducted kinetic studies of reactions between substituted (X) anilines and substituted (Y) phenylmethanesulfonyl chlorides (PSC) and fluorides (PSF), (2).

$$XC_6H_4NH_2 + YC_6H_4CH_2SO_2Z \longrightarrow$$

$$YC_6H_4CH_2SO_2{}^+NH_2C_6H_4X + Z^- \qquad (2)$$

where $X = p\text{-}OCH_3$, $p\text{-}CH_3$, H, p-Cl
$Y = p\text{-}OCH_3$, $p\text{-}CH_3$, H, p-Cl , $p\text{-}NO_2$
Z = F , Cl

In this reaction nucleophilic displacement takes place at sulfur with the halides, F^- and Cl^- , as the leaving group. Experimental second order rate constants (16 values of k_{XY}) obtained by varying substituents both on the nucleophile (X) and the substrate (Y) were subjected to multiple regression analysis[4] using eq (1). The ρ_X, ρ_Y and ρ_{XY} values determined are summarized in Table 1.

The ρ_X and ρ_Y values in Table 1 agree satisfactorily with those given in parenthesis which are obtained using the simple Hammett equation, $\log (k_i/k_H) = \rho_i \sigma_i$, where i = X or Y.

Table 1. The ρ_X , ρ_Y and ρ_{XY} values for reaction (2) in MeOH at 45.0 °C obtained by multiple regression analysis.[4] Values in parenthesis are those obtained by the simple Hammett equation. (CC = multiple correlation coefficient[4])

Z	ρ_X	ρ_Y	ρ_{XY}	CC
Cl	-3.46 (-3.52)	2.16 (2.02)	-0.68	0.999
F	-1.05 (-0.98)	0.93 (1.12)	-1.24	0.999

Relatively large positive ρ_Y values in this table indicate that bond making is ahead of bond breaking at the TS for both substrates.[5] This is in contrast with the contention of Ciuffarin et al.,[6] that sulfonyl fluoride reacts by a different mechanism from other sulfonyl halides ; they argued that sulfonyl halides react by the addition - elimination (S_AN) mechanism involving an intermediate, and bond formation is the rate - determining for sulfonyl halides except fluoride for which bond breaking is the rate determining. Again our mechanistic criteria based on the cross interaction constant ρ_{ij} clearly rule out the possibility of the rate - determining bond cleavage for sulfonyl fluoride, since the rate - determining bond cleavage process requires $\rho_{XY} \cong 0$.[3]

Magnitudes of ρ_X and ρ_Y values for PSC are much greater than those for PSF, indicating much greater charge transfer from N to S in the reaction of PSC at the TS. Hence it *appears* that much greater degree of bond formation is achieved in the reaction of PSC at the TS. However this conclusion is grossly misleading.

Reference to Table 1 reveals that in a striking contrast to the smaller $|\rho_X|$ and ρ_Y values for PSF, the absolute value of the cross interaction constant $|\rho_{XY}|$ for PSF is actually greater than that for PSC. Hence on account of the relative $|\rho_{XY}|$ values, bond making is more advanced for PSF compared with that for PSC.[3] Thus if we had not evaluated the ρ_{XY} values, we would have reached wrong conclusion as to the relative extent of bond making at the TS.

The present results clearly show that the extent of charge transfer is not an indication of bond tightness, i.e., considerable charge transfer does not necessarily mean a tight bond formation.[7] This is true especially in the case of widely varying structures[8] such as for PSC and PSF which have leaving groups that are very much different in their leaving ability.

Shaik and Pross[9] argued that the poor leaving group ability exhibited by F^- has its origins in the poor acceptor ability of C-F bond, which in turn originates in the strong C-F bond. The same argument will also apply to S-F bond relative to S-Cl bond.[10] Theoretical [11] as well as experimental [12] studies have indeed shown that bond making is more complete at the TS for the substrate with the poor leaving group ability.

The More O'Ferrall-Jencks plots [13] also predict that the poor leaving group, F^-, should have greater degree of bond formation in agreement with our conclusion based on the $|\rho_{XY}|$ values.

Relative magnitudes of ρ values in Table 1 clearly demonstrate that extensive charge transfer actually takes place at large intermolecular separation. It is therefore *dangerous* to assess the degree of bond making at the TS by the magnitude of ρ_X and / or ρ_Y values alone.

Full details of the present work will be reported elsewhere.

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