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AN ANALYSIS OF THE BREAKDOWN IN THE SELECTIVITY REACTIVITY PRINCIPLE FOR CATION-ANION COMBINATION REACTIONS

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Some uncertainty has recently been cast on the validity of selectivity reactivity relationships. This uncertainty has resulted from the discovery of instances in which an apparent breakdown in the relationship appeared to occur. The purpose of this communication is to show that such contradictions may be readily rationalised within the current theoretical framework of transition state theory and the Hammond postulate[1] and that the apparent inconsistencies stem from the variable influence of solvent.

Possibly the most disturbing results obtained to date were presented in a series of papers by Ritchie[2] in which the nucleophilic activity of a large number of nucleophiles in their reaction with cations were correlated by:

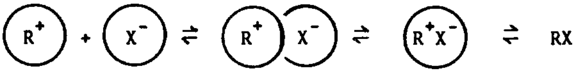
$$\log k_n/k_w = N_+ \qquad (1)$$

where k_n is the rate constant for the reaction of a cation with the nucleophilic system (i.e. a given nucleophile in a given solvent), k_w is the rate constant for reaction of the same cation with water and N_+ is the parameter characteristic of the nucleophilic system.

The remarkable observation that was made by Ritchie was that the value of N_+ for a particular nucleophilic system was independent of the reactivity of the cation involved. This, in spite of the fact that the absolute rate constants for the reaction of the nucleophiles with the different cations extended over six orders of magnitude. This result is clearly at odds with the basic tenet that the selectivity of a substrate in its reactions with competing reagents is inversely proportional to its reactivity. By inference, the validity of the Hammond postulate which forms the basis of the selectivity reactivity principle is also questioned.

Ritchie interpreted the constant N_+ value as indicating the degree of desolvation that the particular nucleophile must undergo in order to react with the cation substrate. This would be an adequate description were the nucleophile desolvation process rate determining. However the large differences in absolute rate constants for different cations indicate that this cannot be the whole story. The situation is further clouded by the conclusion reached by Ritchie, that in the transition state, cation desolvation has not begun. If this were the case then it would be anticipated that the absolute rate constants would be cation independent, contrary to experimental fact. The basis for this conclusion was the apparent lack of rate-equilibrium and equilibrium-equilibrium correlation. As a result, Ritchie deduced that the difference in cation solvation in different solvents varied for different cations. Since equation (1) described the behaviour of cations in different solvents, it was concluded that cation solvation in the ground and transition states are essentially identical.

While accepting that the lack of rate-equilibrium and equilibrium-equilibrium correlation does indicate differential cation solvation we suggest that the conclusion that ground and transition state cation solvation are equal is incorrect and that the rate-rate correlation may be readily rationalised according to the following scheme:



Separate solvated ions react to form a solvent separated ion pair in which the anion has undergone partial desolvation. The solvent separated ion pair reacts further in the rate determining step to form an intimate ion pair. This step involves the partial desolvation of the cation. Finally, the intimate ion pair collapses to form the product.

The following analysis shows the reason for the absence of selectivity in the reactions of different cations with various nucleophilic systems.

$$\Delta G^{\ddagger}_{S_1}(N_1)(C_1) = \alpha_1 G_{S_1}(N_1) + \beta_1 G_{S_1}(C_1) \tag{2}$$

$$\Delta G^{\ddagger}_{S_2}(N_2)(C_1) = \alpha_2 G_{S_2}(N_2) + \beta_1 G_{S_2}(C_1) \tag{3}$$

where $\Delta G^{\ddagger}_{S_1}(N_1)(C_1)$ is the free energy of activation for reaction of cation (1) with nucleophile (1) in solvent (1), $G_{S_1}(N_1)$ is the free energy of solvation of nucleophile (1) in solvent (1), $G_{S_1}(C_1)$ is the free energy of solvation of cation (1) in solvent (1) and α and β represent factors whose value varies between 0 and 1 and whose magnitude therefore indicates the degree of desolvation in the transition state. Subtracting eq. (2) from (3):

$$\Delta\Delta G^{\ddagger}(C_1) = \alpha_2 G_{S_2}(N_2) + \beta_1 G_{S_2}(C_1) - \alpha_1 G_{S_1}(N_1) - \beta_1 G_{S_1}(C_1) \tag{4}$$

where $\Delta\Delta G^{\ddagger}(C_1)$ represents the free energy difference between the free energy of activation of cation (1) with two nucleophilic systems. In similar fashion:

$$\Delta\Delta G^{\ddagger}(C_2) = \alpha_2 G_{S_2}(N_2) + \beta_2 G_{S_2}(C_2) - \alpha_1 G_{S_1}(N_1) - \beta_2 G_{S_1}(C_2) \qquad (5)$$

where $\Delta\Delta G^{\ddagger}(C_2)$ is the difference in the free energy of activation for cation (2) with the same two nucleophilic systems. Subtracting eq. (4) from (5):

$$\Delta\Delta G^{\ddagger}(C_2) - \Delta\Delta G^{\ddagger}(C_1) = \beta_2[G_{S_2}(C_2) - G_{S_1}(C_2)] - \beta_1[G_{S_2}(C_1) - G_{S_1}(C_1)] \qquad (6)$$

Now the constant selectivity observed by Ritchie may be expressed as:

$$\Delta\Delta G^{\ddagger}(C_2) - \Delta\Delta G^{\ddagger}(C_1) = 0$$

i.e. $\beta_1[G_{S_2}(C_1) - G_{S_1}(C_1)] = \beta_2[G_{S_2}(C_2) - G_{S_1}(C_2)]$

or more generally:

$$\beta(G_{S_2} - G_{S_1}) = \text{constant} \qquad (7)$$

This final equation merely states that the degree of desolvation for a particular cation in the transition state is inversely proportional to the difference in solvation energy of that cation in two solvents. If the reasonable assumption, that $G_{S_2} - G_{S_1}$ is proportional to the solvation energy, is made, then the outcome is readily comprehensible. In simple terms it states that for a series of cations to show no selectivity in their reaction with pairs of nucleophilic systems, reactive and therefore strongly solvated cations (i.e. large $G_{S_2} - G_{S_1}$) will undergo only slight desolvation in the transition state (β close to 0) while for unreactive and therefore weakly solvated cations (i.e. small $G_{S_2} - G_{S_1}$) will undergo considerable desolvation in the transition state (β close to 1). This conclusion is readily justified by the Hammond postulate since the conclusion may be rephrased so as to state that a reactive cation will produce a reactant like transition state which is still considerably solvated.

This scheme is supported by the conclusion reached by Atkinson[3] that formation of the one solvent separated ion pair is anion dependent, while formation of the intimate ion pair is cation dependent and anion independent.

The lack of selectivity may therefore be viewed as the cancellation of two opposing effects. On the one hand a reactive cation is strongly solvated, a factor which would tend to increase selectivity. On the other hand the transition state for a reactive cation is reactant like, resulting in a decrease in selectivity. In the absence of complicating solvent effects, this latter influence operating alone would produce the normal reactivity selectivity relationship.

We should point out that this derivation assumes that the degree of desolvation for a particular cation in different solvents is the same. While this may be a crude assumption, a more complex derivation based on a more subtle assumption that the ratio of desolvation factors for a cation in different solvents does not equal 1, as it does in the crude assumption, but remains constant for all cations, is possible. For simplicity it has not been presented here and will be discussed in a full publication.

The conclusion to be drawn therefore is that reactivity selectivity relationships will operate as expected by theroretical considerations under ideal conditions only. In practice, solvent effects play a substantial though often subtle role in reaction mechanism, thereby alluding to apparent inconsistencies within the theoretical framework.

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