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ON THE COEXISTENCE OF THE "REACTIVITY-SELECTIVITY" AND THE "CONSTANT SELECTIVITY" RELATIONSHIPS IN REACTIONS OF CARBONIUM IONS WITH NUCLEOPHILES

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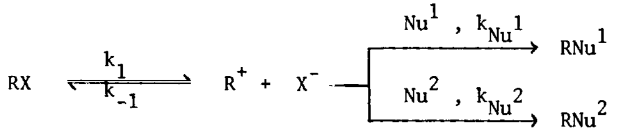
Abstract: It is noted that the "reactivity-selectivity" and the "constant selectivity" relationships for the R^+ + Nu reactions can coexist if diffusion-controlled rates for one nucleophile govern the behaviour at the reactivity-selectivity region.

Two apparent contradictory rules govern the selectivities of carbonium ions R^+ in their reactions with nucleophiles. For the reactions of two nucleophiles Nu^1 and Nu^2 with solvolytically generated R^+ from RX (eq 1) the reactivity-selectivity principle (RSP) is applicable since the selectivity S = $\log(k_{Nu}1/k_{Nu}2)$ increases with decreased reactivity of R^+.[1-7] Since R^+ is formed in steady state concentrations and k_{Nu} cannot be measured, $\log k_1$ is taken as a measure of the reactivity of R^+ by applying Hammond's postulate and an inverse stability-reactivity relationship for R^+. The S values for different RX species are measured by two methods : (a) From the product ratio in a competitive reaction of Nu^1 and Nu^2 which gives eq 2 , and LFER between $\log k_1$ and $\log(k_{EtOH}/k_{H_2O})$ in 70% EtOH,[5,6] or $\log(k_{N_3^-}/k_{H_2O})$ in 80% acetone[3,4] were found. (b) When the solvolysis produces a long-lived R^+, analysis of the common ion rate depression by the leaving group X in a solvent SOH gives the k_{X^-}/k_{SOH} ratios.[7] Reactivity-selectivity relationships were found for Cl^- vs. H_2O as nucleophiles in solvolyses of benzhydryl halides[7] and for Br^- vs. 2,2,2-trifluoroethanol or vs. AcO^- in the solvolyses of α-arylvinyl bromides.[8]



$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+ + X^- \begin{cases} \xrightarrow{Nu^1,\ k_{Nu}1} RNu^1 \\ \xrightarrow{Nu^2,\ k_{Nu}2} RNu^2 \end{cases} \qquad (1)$$

$$k_{Nu}1/k_{Nu}2 \;=\; [RNu^1]x[Nu^2]/[RNu^2]x[Nu^1] \qquad (2)$$

In contrast, Ritchie and coworkers in recent years measured directly many k_{Nu} values for reactions with stable triarylmethyl , aryltropylium and aryldiazonium cations and found that while $k_{Nu}1$ changes strongly with the structure of R^+ , the S value for any pair of nucleophiles in one solvent remains constant regardless of the structure of R^+.[9-11] The selectivity of Nu^1 vs. water was defined as N_+ (eq 3) - a characteristic nucleophilic parameter.[9,10] This "constant selectivity"

$$\log(k_{Nu}1/k_{H_2O}) = N_+ \qquad (3)$$

relationship holds not only for stable R^+'s but also for reactions at other electrophilic centers such as sulfonyl sulfur,[12a] C=O,[10b] and activated aromatic[12b] and vinylic[12c] carbons.

The two selectivity rules seem to be incompatible. Pross[13] showed that a constant selectivity can be obtained if the fractional desolvation of R^+ in the transition state is smaller for the more solvated electrophile and argued that such behaviour is a reflection of the RSP. Ritchie [10a] noted that according to Winstein's solvolysis scheme[14] the solvolysis products may be formed from several cationoid species. Consequently, the S values calculated by eq 2 measure an average selectivity of the various product-forming intermediates and are not directly comparable with the N_+ values. He demonstrated a change in S with $[NaN_3]$ which was ascribed to this phenomenon.[15] Harris discussed the RSP in relation to this question.[16] Ion pairs are certainly involved in the solvolyses of some of the compounds used for establishing the RSP. However, by measuring the selectivities from the kinetic data on common ion rate depression (method b above) in the solvolyses of several α-arylvinyl systems where products are formed only from the free ions, a log k_1 vs. S relationship was still found.[8,17]

We believe that the two selectivity rules are not necessarily contradictory. As with other LFER they may represent different regions of a non-linear reactivity-selectivity plot since the stabilities of the ions obeying the RSP and those obeying eq 3 are much different. The assumption that free cations are involved in the $R^+ + Nu$ reaction in both Ritchie's and the reactivity-selectivity range can lead to the observed log k_1 vs. S relationship without contradicting eq 3. This is demonstrated below with the aid of the $k_{N_3^-}/k_{H_2O}$ ratios for which more data are available than for reactions with other pairs of nucleophiles.[18]

Sneen , Schleyer and coworkers[3,4] have found a linear log k_1(RCl) vs. log $(k_{N_3^-}/k_{H_2O})$ $(S(N_3))$ plot which covers thirteen log k_1 units and three S units. The least selective compound is 2-adamantyl chloride $(S(N_3) = 0.23)$ and the most selective is trityl chloride $(S(N_3) = 3)$.[19] The $N_+(N_3^-)$ value in water is 7.66 [10b] when the water concentration is not taken into account and therefore $k_{N_3^-}/k_{H_2O}$ toward the stable cations is 9.40. Since $N_+(N_3^-)$ is higher in DMSO and in MeOH than in water[10b] the S value is probably ≳ 9.40 in 80% acetone. Consequently, the most stable cations give the highest selectivity.

The least stable cation for which k_{H_2O} was measured directly is $AnCPh_2^+$ where $k_{H_2O} = 10^3\ M^{-1}s^{-1}$.[20] The k_{H_2O} values are nearly additive for $AnCPh_2^+$, An_2CPh^+ and An_3C^+ ,[20] giving k_{H_2O} of ca. $10^4\ M^{-1}\ s^{-1}$ toward Ph_3C^+. The $k_{H_2O}/k_{N_3^-}$ ratio for An_3C^+ is ca. $2.5x10^7$.[21] If we assume that the same constant selectivity holds for other Ar_3C^+ ions , $k_{N_3^-}$ is calculated to be ca. $2.5x10^{11}\ M^{-1}s^{-1}$ for Ph_3C^+. This calculated value is higher than the diffusion-controlled value. Since all the compounds on the Sneen-Schleyer plot (e.g., benzhydryl, t-butyl , norbornyl and adamantyl chlorides)[3,4] give more reactive ions than Ph_3C^+ , all their $k_{N_3^-}$ values will also be diffusion-controlled, i.e., nearly the same. If Hammond's postulate holds for the reactions of R^+ with H_2O , k_{H_2O} will increase, i.e., $k_{N_3^-}/k_{H_2O}$ will decrease on increasing the ion reactivity as measured by a lower k_1. A reactivity-selectivity relationship will result and the linearity of the Sneen-Schleyer plot suggests that log k_{H_2O} is linear in log k_1(RCl). In this case the k_{H_2O} values for the derived cations are obtained directly from the values of S and the diffusion-controlled $k_{N_3^-}$. This calculation gives a k_{H_2O} value of 10^6-10^7 for Ph_3C^+ in water, higher than that estimated above. This is understood in view of the different solvents and the problems associated with the $S(N_3)$ value for Ph_3C^+,[19] and the extrapolation used above.[18,20]

A similar behaviour is demonstrated by the reactions of $PhCH_2^+$, Ph_2CH^+ and Ph_3C^+ cations with nucleophiles in 1,2-dichloroethane.[22] The reactions of the three cations with Br^- and I^- are diffusion-controlled.[22a] The reactions with neutral nucleophiles such as Bu_3N or water are slower and the k_{Br^-}/k_{Bu_3N} ratios (13500 for Ph_3C^+ , 104 for Ph_2CH^+ and 52 for $PhCH_2^+$)[22a,c] or the k_{Br^-}/k_{H_2O} ratios (40000 for Ph_2CH^+ and 2900 for $PhCH_2^+$)[22a,b] calculated from these values give an apparent selectivity-stability relationship similar to those observed in solvolysis , for the reasons outlined above.

The selectivity-reactivity relationships observed for solvolysis reactions result therefore from a stability-reactivity relationship for the reactions of various R^+'s with a single nucleophile. Combined with Pross' explanation for the stable ions, the stability-reactivity relationship can account for the behaviour of both solvolytically generated and stable cations. Some of Ritchie's ions (e.g., tris(p-dimethylaminophenyl)methyl or substituted tropylium) are so stable that RX is ionic and the hypothetical $RX \longrightarrow R^+X^-$ reaction is exothermic. In contrast, the solvolytic generation of carbonium ions is usually an endothermic process. Since the transition states of the reactions of various substrates in a reaction series which follows a LFER are usually close to one another along the reaction coordinate axis, a log k_1 vs. S relationship should not a priori hold for both classes of ions together.

Regardless of the validity of our explanation for the reactivity-selectivity relationship for reactions of N_3^- vs. H_2O,a complete reactivity-selectivity plot for a pair of nucleophiles should exhibit three different regions: (a) A non-selectivity region (S = 0) where both nucleophiles react with R^+ by diffusion-controlled rates. This question was discussed by Schleyer in relation to the Sneen-Schleyer plot at the region of the most reactive cationoid species.[4] (b) A reactivity-selectivity region where one of the nucleophiles reacts by a diffusion-controlled rate and the other by a lower rate and $S < S_{max}$. This region will be frequently encountered in comparisons of reactive anionic nucleophiles (e.g., N_3^-) with relatively non-reactive neutral nucleophiles such as the solvent SOH. (c) A constant selectivity region where the rates are below the diffusion controlled limit and S is at its maximum value (S_{max}). This region will be mostly encountered in comparisons of relatively non-reactive neutral nucleophiles such as the solvent components in a binary solvent mixture, e.g. , when $Nu^1 = H_2O$ and $Nu^2 = EtOH$.[5,6,16] The limits of the regions to which each ion belongs depend on the nucleophiles compared. For example, with the two very reactive nucleophiles PhS^- and N_3^- both benzenediazonium ion and tolyldiazonium ion belong to region (c) since they behave according to eq 3 and $S = S_{max} = 2.2$ in MeOH. The stable p-nitrobenzenediazonium ion belongs, however, to region (a) since $S \sim 0$.[9]

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