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ON THE REACTIVITY-SELECTIVITY RELATIONSHIP IN THE SOLVOLYSIS OF SEVERAL REACTIVE ALKYL HALIDES

Rachel Ta-Shma and Zvi Rappoport*
Department of Organic Chemistry
The Hebrew University, Jerusalem 91904, Israel

SUMMARY: In contrast to previous reports, the selectivities of four carbenium ions R^+ towards N_3^- and H_2O ($\log(k_{N_3^-}/k_{H_2O})$) change more than the solvolytic reactivities ($\log k_{solv}$) of their rather reactive precursors RCl.

In the study of the operation of the reactivity-selectivity principle (RSP)[1,2] in carbenium ion reactions it is customary to plot the logarithm of the solvolysis rate ($\log k_{solv}$) of RX against the selectivity S in the competitive capture of the cation by two nucleophiles N^1 and N^2 ($S = \log(k_{N^1}/k_{N^2})$). The most extensive plot of this type involves $\log k_{solv}$ for alkyl chlorides (RCl) against the selectivity of R^+ towards the pair of nucleophiles N_3^- and water ($S_{N_3^-} = \log(k_{N_3^-}/k_{H_2O})$). The plot is reasonably linear for alkyl chlorides covering the range from 1-adamantyl chloride to Ph_3CCl[3a,b] with a slope $m = \log k_{solv}/S_{N_3^-} \geq 2.4$.[3,4] The least reactive compound — 2-adamantyl chloride — deviated seriously from the line.

A higher $\log k_{solv}$ value is assumed to be associated with a higher stability of R^+. Hence, the plot represents a stability-selectivity or a reactivity-selectivity behaviour. However, it was previously suggested that for most of the substrates of this plot the reaction with azide ion is diffusion-controlled.[5]

It is expected that at both ends of the linear region there are extended regions of constant selectivity. At one extreme, for a very sluggish RCl the derived R^+ is so reactive that its reactions with both azide ion and water are diffusion controlled, i.e., $S_{N_3^-} = 0$. An approach to this value is observed for 2-adamantyl.[3b] At the other extreme, there are the very stable cations, for which Ritchie[6] showed that the S values are constant (N_+) regardless of the cation. While $\log k_{solv}$ for most of the precursors RCl in this region are unknown, it is reasonable that for at least some of them, they also increase with the stability of the ion. Consequently, a very extended $\log k_{solv}$ vs. $S_{N_3^-}$ plot should consist of a central linear region with $m > 1$, flanked by two regions at high and low S values where $m = \infty$. Different shapes of the curve between these well defined regions could be envisioned. For example, the linear parts with $m > 1$ and $m = \infty$ may intersect sharply with no border region.

An interesting situation may arise if the shape of the $\log k_{solv}$ vs. $S_{N_3^-}$ plot is sigmoid.

In this case, in the border region the m value will be low. If $m < 1$ this will be a region where the selectivity will increase more than the reactivity. Such behaviour was found in vinylic solvolysis.[7] The difference in the k_{solv} values for several α-anisyl-β,β-disubstituted vinyl bromides were smaller than the selectivity differences for capture of R^+ by Br^- vs. AcO^- or by Br^- vs. CF_3CH_2OH. An explanation involving steric reasons was invoked.[7]

We report here analysis of literature data for four reactive systems at the border with Ritchie's region. The calculations of log k_{solv} and $S_{N_3^-}$ values require extrapolations for substituent, leaving group, solvent and temperature effects and the details of the extrapolations are given in Table I. Also given are previous values for the same systems.[3b] It is clear that the selectivity increases faster than the reactivity.

It should be noted that three of the points are the upper points on the previous stability-selectivity line with $m = 3.8$.[3b] Those for Ph_3CCl and p-TolCH(Cl)CH=CHCH$_3$ are on the line while the point for PhCH(Cl)CH=CHCH$_3$ deviates.[3b] The three points are also on a previous linear plot with $m = 2.4$.[3a] The reasons why the same raw data leads to a different behaviour by the previous workers and by us is two-fold. First, Schleyer and coworkers[3b] used Hill's data[8] for Ph_3C^+ but in calculating $S_{N_3^-}$ they forgot the water concentration in 80% acetone and their value should be 11.2-fold larger. Moreover, we used Swain's higher value[9] which seems more in line with Hill's value for Ph_3COAc, the substrate that shows the least complications due to mixing problems.[8] Second, with the allylic compounds k_{solv} is known only for the p-nitrobenzoates. Previous estimation[3b] of k_{solv}(RCl) used a k_{Cl}/k_{OPNB} ratio of 3.10^4 as found for the t-BuX system.[10] However, since the reactivity of the compounds is closer to that of the Ph_2CHX system we used a value of $4.4 \cdot 10^5$ (as found for Ph_2CHX[11]) which seems more appropriate.

The only system which does not appear in the previous plot is p,p'-dimethoxybenzhydryl chloride (An_2CHCl). Both k_{solv} and $S_{N_3^-}$ are not available in 80% acetone and require extensive extrapolations. The k_{solv} values for p-$RC_6H_4CH(Ph)Cl$ (R=H, Cl, t-Bu) at 25° together with that for (p-Tol)$_2$CHCl which was extrapolated from 0°[15,17] gave a linear log k_{solv} vs. $\Sigma\sigma^+$ plot with $\rho^+ = -4.01$ ($r = 0.99998$) in 80% acetone at 25°. From the relative k_{solv} values which are available for other Ar_2CHCl systems[18] we calculated $\rho^+ = -4.08$ ($r = 0.990$) for 4 substituents with $\Sigma\sigma^+$ between 0.79 and -0.18 in 70% acetone, and $\rho^+ = -3.08$ for 7 substituents with $\Sigma\sigma^+ = -0.78 - -1.56$ in 85% acetone at 0°. Since it is possible that ρ^+ decreases with the reactivity and the change occurs mid-way between Ph_2CHCl and An_2CHCl, we calculated k_{solv} for the latter from that of the former and the average ρ^+ value of -3.54. The selectivity was calculated from the data for the corresponding mesitoate[16] with appropriate corrections (see Table I).

Table I shows that at the border region between Ritchie's constant selectivity region and the apparent reactivity-selectivity region of Sneen and Schleyer and coworkers[3a,b] the selectivity changes as much or even more than the reactivity. The behaviour is irregular but for the four substituents a reactivity range of one log unit is associated with a selectivity change of ca. 3 log units.

This behaviour can be viewed as representative of a sigmoid part of an extended reactivity-

Table I. Log k_{solv} and $S_{N_3^-}$ Values for Several Activated Alkyl Chlorides

Compound	log k_{solv} , sec^{-1} (80% Me_2CO, 25°)	$S_{N_3^-}$ (T, °C)	log k_{solv} ($S_{N_3^-}$) from ref. 3b
$PhCH(Cl)CH{=}CHCH_3$	0.31 [a]	2.15 (25)[b]	-0.87 (2.11)
p-$TolCH(Cl)CH{=}CHCH_3$	1.35 [a]	3.09 (65)[c]	0.20 (2.91)
Ph_3CCl	0.95 [d]	5.00 (-34,25)[e] or 4.05 (30)[f] or 4.65 (30)	0.94 (3.00)
An_2CHCl	1.37 [h]	4.95-5.23 (26)[i]	

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[a] Calculated (as in ref. 3b) from the sum of k_{solv} + $k_{rearrangement}$ for the corresponding p-nitrobenzoate in 60-80% dioxane at 25° [12] using a k_{Cl}/k_{OPNB} ratio of $4.4 \cdot 10^5$.

[b] Average value from the product distribution in 60% dioxane. [13]

[c] The average value from the product distribution of the allylic isomer in MeOH [13] was corrected by a factor of 1.88 which reflects the difference between the $k_{N_3^-}/k_{MeOH}$ ratios of the two phenylallyl isomers.[13,14] The $S_{N_3^-}$ value was calculated from the corrected value using the relationship $S_{N_3^-}/(k_{N_3^-}/k_{MeOH})[MeOH] = 93$ as found for the phenylallyl system.

[d] Calculated from the values in 85% acetone (assuming a Grunwald-Winstein m value of 1.0) at -34° and -14°C. [9]

[e] In 85% acetone at -34° and in 92% acetone - 2% dioxane - 6% water at 25°. [9]

[f] From the products of Ph_3CCl in 80% acetone at 30°. [8]

[g] From the products of Ph_3COAc in 80% acetone at 30°. [8]

[h] Calculated from the value for Ph_2CHCl [15] and the average ρ^+ value (see text).

[i] Calculated from the $k_{N_3^-}/(k_{MeOH}[MeOH])$ values for $An_2CHOCOC_6H_2Me_3$-2,4,6 [16] which were multiplied by a factor of 93 (cf. footnote c). The values decrease ca. 2-fold on changing $[NaN_3]$ from 10^{-5} M to 10^{-3} M.

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selectivity plot as discussed above. This suggestion is in line with the results of an extensive reanalysis of the log k_{solv} against the $S_{N_3^-}$, which will be discussed in a future publication. [19] At present, we want to emphasize the fact that the points of Table I previously belonged to the linear part of the reactivity-selectivity plot with an m value of 3.8. This is disturbing since our extrapolations were exactly of the same type used by the previous workers. [3] Our main conclusion from Table I is therefore that extreme caution should be exercised in deducing linearity of reactivity-selectivity plots which are based on long range extrapolations. This conclusion concerns the method by which the plot is constructed and is not related to the question of the validity of the RSP.

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