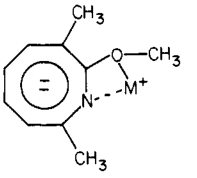

I

HMPA. This would explain the larger K_{disp} for DMMA$^{-}\cdot$ than for COT$^{-}\cdot$.

Conclusions

The spin distribution in the DMMA anion radical (free of ion association) is similar to that of a monosubstituted COT anion radical, where the substituent acts as an extension of the π conjugation (i.e., a phenyl group). The dianion of DMMA readily ion pairs with metal cations in solvents other than HMPA, which drives the disproportionation far to the right and accounts for the fact that the DMMA anion radical has not been observed prior to this report. The stabilities of the dianions of DMMA and TBCOT are enhanced by the interaction of the cation with the nitrogen and/or oxygen atoms in the solid state. The crystal lattice energies of these solid dianion salts appear to play a more dominant role in controlling the heats of formation from the neutral molecules and sodium metal than do aromaticity considerations and the effect of the nitrogen upon the aromatic character of the dianion.

Experimental Section

X-band ESR spectra were recorded on a Varian E-4 spectrometer that is interfaced to a 64K MINC II computer system. The temperature was controlled within ±2 °C with a Varian V-4557 variable temperature controller, which was calibrated with an iron-constantan thermocouple.

Solvent-free dianion salts were prepared as previously described,[11] and they were placed into thin-walled evacuated glass bulbs. To ensure that no THF was left in the dianion salts, D_2O was added and the solution submitted to NMR analysis. No THF was found in the D_2O. Other glass bulbs were broken under 100 mL of water in a modified cell of a Parr solution calorimeter.[6] The data collection, analysis of the calorimeter contents, and calorimeter apparatus were exactly as previously described.[6]

The anion radicals were generated via alkali-metal reduction in freshly distilled HMPA under high vacuum as described earlier.[5] After complete dissolution of the metal mirror, an ESR sample was sealed off from the apparatus. Two samples (one from a COT reaction and one from a DMMA reaction) were compared for spin concentration. The ESR data were collected with the maximum modulation amplitude as described by Goldberg[12] to minimize the error in obtaining the relative anion radical concentration from the double integral of the ESR signal. The ESR data were sent directly into the computer for double integration, and the numerical value obtained from the computer was used for A. Since the DMMA anion radical solutions were slowly decomposing, a correction had to be applied to A to account for this loss of anion radical. The half-life of the anion radical in HMPA is 23 min at 0 °C. This short half-life, coupled with the fact that 1-h scan times are necessary to record a well-resolved spectrum containing over 3000 ESR lines, makes it impossible to record a full well-resolved spectrum.

The DMMA was synthesized by the method of Paquette and coworkers.[13] The purity of the final fractionally distilled product was found to be greater than 98% via VPC and NMR analysis.

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Registry No. DMMA anion radial, 69134-59-4; DMMA dianion, 86709-88-8.

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Azide-Water Competition in Solvolysis Reactions. A Revisit of the Reactivity-Selectivity Relationship[1,2]

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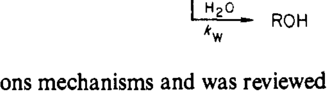
Abstract: The suggested linearity between the logarithms of the solvolysis rate constant (k_{solv}) of RX and the selectivity (k_N/k_W) in capture of the intermediate cation R^+ by water (W) and N_3 (N) in 80% acetone was reinvestigated by using extended literature data. The assumptions involved in deriving the k_N/k_W values, such as first-order dependency on the nucleophile concentration in its reaction with R^+ and the temperature, solvent, nucleofuge, and other extrapolations required for obtaining the parameters, were discussed. The extended log k_{solv} vs. log (k_N/k_W) plot, which is based on the revised set of values, is not linear and composed of five regions: (a) Ritchie's constant selectivity region; (b) a border region where the selectivity increases more than the reactivity and which may be an artifact; (c) an apparent reactivity-selectivity (RS) region with an appreciable scatter of the points, where log (k_N/k_W) decreases on decreasing k_{solv} (the reaction with N_3^- in this region is diffusion controlled and the plot reflects a log k_{solv} vs. log k_W relationship); (d) a low k_{solv} and nearly constant low selectivity region where hindrance to nucleophilic approach to the intermediate may sterically enforce a preassociation ion pair mechanism on the reaction; (e) an inverted RS region, where the selectivity increases on decreasing k_{solv} and where the reaction with N_3^- is mostly S_N2. The various mechanistic regions were discussed in relationship to the existence and the lifetimes of the cationoid intermediates.

According to the reactivity-selectivity principle (RSP), in a series of similar reactions the less reactive reagent shows the highest selectivity. The principle is used extensively in the study of organic reactions mechanisms and was reviewed recently several times.[3,4b,c] However, many examples contradicting the RSP

Scheme I



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(1) Presented in part at the Euchem Conference on Correlation Analysis in Organic Chemistry (CAOC II), July 18-23, Hull, England, Abstract 0/19.

(2) Preliminary communications: (a) Ta-Shma, R.; Rappoport, Z. *Tetrahedron Lett.* **1982**, *23*, 781. (b) Rappoport, Z.; Ta-Shma, R. *J. Org. Chem.* **1982**, *47*, 5207.

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started to accumulate recently,[4–6] the principle was strongly criticized,[4c,6a,g] and it was suggested[6a] " that the RSP should be abandoned as a general principle".

The RSP was applied frequently with some success in S_N1 reactions.[3a] On the assumption that $k_{\text{solvolysis}}$ (k_{solv}) reflects carbocation stability and reactivity[7] (i.e., the faster solvolysis gives the more stable carbocation that reacts more slowly with a nucleophile), a relationship between carbocation stability and its selectivity toward a pair of nucleophiles was found. Pairs of nucleophiles studied involved the solvent (e.g., H_2O or AcOH) and Cl^-,[8] H_2O and EtOH,[9] and H_2O and N_3^-.[10,11]

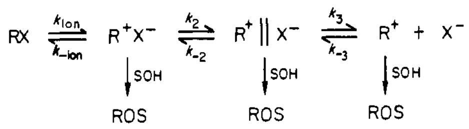
Sneen and co-workers[10] plotted log k_{solv} for a series of alkyl chlorides (RCl) in 80% acetone at 0 °C vs. the selectivity measure log (k_N/k_W), where k_N and k_W are the second-order constants for the reactions of the derived cationoid species R^+ with N_3^- and H_2O respectively, and their ratios were measured by applying Scheme I and the derived eq 1. They found a linear log k_{solv} vs.

$$k_N/k_W = (\%\ RN_3)[H_2O]/((\%\ ROH)[N_3^-]) \qquad (1)$$

log (k_N/k_W) relationship with a slope of 2.83 for seven substrates, ranging from t-BuCl to Ph_3CCl. Raber, Harris, Hall, and Schleyer (RHHS)[11] extended this study by adding new and literature data. A plot of log k_{solv} in 80% acetone at 25 °C vs. log (k_N/k_W) for 16 compounds gave a reasonable straight line with a slope of 3.8 covering 13 powers of ten in k_{solv} and three powers of ten in selectivity. They also discussed several failures and limitations of the relationship.

The RHHS relationship was quoted several times as an important example of the RSP in solvolysis reactions and was used in mechanistic studies.[3a,9e–h,12a–h] However, various aspects of Sneen's and the RHHS work were criticized. Songstad and co-workers[12i] questioned the applicability of N_3^- as a solvolysis probe. Harris and co-workers[9b] commented that Sneen's treatment assumes that R^+ is a free cation, whereas ion pairs are involved in the solvolysis of many of the systems studied, and Dorfman and co-workers[12j] suggested that k_{solv} is not a good measure of the ion reactivity.

Scheme II



The actual k_N/k_W values were rarely used. For example, Sneen's value[10] for t-BuCl was quoted[12e,13] without reference to RHHS's different value.[11] Sunko and co-workers[14] calculated k_N/k_{SOH} values from the RHHS data in 80% EtOH.[11] Kevill and Kim[15] noted that the RHHS order k_N/k_W(1-adamantyl) > k_N/k_W(2-adamantyl)[11] will be reversed when calculating k_N/k_{EtOH} ratios and concluded that points for the adamantyl systems should be omitted from the RS line. Pross and co-workers[9e,g] plotted Harris' log (k_{EtOH}/k_W) values[9b] against RHHS' log (k_N/k_W) values for the same compounds and found a linear relationship with a unit slope in contradiction with the RSP.[2b]

A main problem results from Ritchie's work. Ritchie and co-workers found that the directly measured reaction rates of different stable cations with the same nucleophile (k_{Nu}) differ greatly, but the selectivities toward pairs of nucleophiles were constant and independent of the nature of R^+.[5] This is expressed by the "constant selectivity relationship" (eq 2) where N_+ is the

$$\log (k_{Nu}/k_{H_2O}) = N_+ \qquad N_+ = \text{constant} \qquad (2)$$

relative nucleophilicity of a nucleophile compared with water, i.e., a selectivity measure. In spite of a suggested modification[16] deviations from eq 2 are usually small,[17] and apparently both eq 2 and the RSP behavior found by Sneen and RHHS coexist for reactions of carbenium ions with nucleophiles. However, the RHHS relationship and eq 2 are mutually exclusive only if they apply to the same series of carbenium ions, but whereas Ph_3C^+ is the most stable cation on the RHHS line, eq 2 was observed for cations that are more stable than Ph_3C^+. Moreover, k_{solv} values for RCl's whose R^+'s obey eq 2 are not available, and there are no directly measured k_N and k_W values for any of the RHHS compounds. This may suggest several explanations for the coexistence of the two relationships: (a) Equation 2 is a special case of the RSP.[18] (b) All of Ritchie's compounds have the same log k_{solv}. This is highly unlikely for Ar_3CCl, ArN_2Cl, and tropylium chlorides and requires positive Hammett ρ values for the equilibrium ionization of Ar_3COH, in contrast with the available data.[19b] (c) The selectivity calculated from the directly determined k_N and k_W may differ from that obtained from the competition method; e.g., a general base catalysis by N_3^- could increase k_W in the competition experiment over its value in the absence of N_3^-. There is evidence for general base catalysis in the $R^+ + Nu^-$ reaction.[5b,19a,c–g] Application of indirect kinetic methods, such as common ion rate depression or solvolysis-exchange in solvent SOH, for calculating analogous k_{Cl}/k_{SOH} and k_{Br}/k_{SOH} selectivity ratios,[20–23] showed that these values for Ar_2CHCl in aqueous

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acetone[21a] or for several ring-substituted vinyl bromides in AcOH[23] or in TFE,[23a] where interference from ion pairing is minimal,[23c] depend on k_{solv} in accordance with the RSP. However, the RSP fails on increasing the steric hindrance to nucleophilic approach to the vinylic system.[8b] (d) Ritchie's cations are free and differ in selectivity from the solvolytically generated intermediates of the RS plots that are ion pairs.[12d]

A more likely rationalization for the discrepancy of the two selectivity relationships was recently invoked.[6a,24,25a] The reactions of the more stable ions obeying eq 2 are activation controlled, whereas less stable cations (e.g., those on the RHHS plot) react with N_3^- by diffusion-controlled rate. Hence, the RHHS relationship reflects a log k_{solv} vs. log k_W relationship, rather than RSP. Indeed, extrapolation of the directly measured k_W and k_N values to reactions of N_3^- with ions less stable than Ph_3C^+ gives k_N values above the diffusion-controlled value.[24b]

Consequently, there are apparently phenomenologically and mechanistically different regions in the log k_{solv} vs. log (k_N/k_W) plot for the N_3^-–H_2O pair. In view of this, the increasing criticism of the RSP, and the different slopes of log k_{solv} vs. log (k_N/k_W) plots[10,11] it seems interesting to revise and extend the Sneen–RHHS relationships. Hence, we analyze in detail below all the literature data known to us on the N_3^-–H_2O competition in solvolysis reaction. We first discuss general problems involved in calculations of the reactivity and selectivity values, and then we demonstrate the problems by comparing our recalculated values with those reported previously. We then present our revised data, together with new literature values and discuss the shape of the extended log k_{solv} vs. log (k_N/k_W) plot in mechanistic terms.

Analysis of Literature Data

Trying to construct a RS plot using k_{solv} and k_N/k_W values derived from product distribution raises three questions: (a) What is the validity of the assumptions that (i) k_{solv} of RCl measures the ionization rate of RX and (ii) k_{solv} is inversely related to the reactivity of the cationoid species (R^+), which is involved in the competitive product formation with N_3^- and H_2O? (b) To what extent are the assumptions involved in deriving eq 1 from Scheme I correct? (c) What are the extrapolations involving solvent, temperature, ionic strength, nucleofuge, and other effects that will give the best k_{solv} and k_N/k_W values? Analysis shows that the literature k_{solv} and k_N/k_W values obtained from different sources and by different methods are not always consistent.

The questions are connected. For example, if products are formed from both free ions and ion pairs their relative distribution and presumably the overall selectivities may depend on the solvent or the nucleofuge. Moreover, different intermediates can be captured at different regions of the mechanistic spectrum, and extrapolation from one region of the plot to another one requires caution.

Problems Associated with the Reactivity Term. Scheme I involves only a free carbenium ion intermediate,[8a] but since in the majority of the solvolyzing systems reversibly formed ion pairs are kinetically important[26] (Scheme II),[27] the measured k_{solv} is composite. When the ion pair return is extensive, $k_{solv} \ll k_{ion}$, and when it is low, $k_{ion} \sim k_{solv}$. The solvolysis of many compounds for which data were analyzed involve ion pair return, but although apparent measures of k_{solv}/k_{ion} values are sometimes available,[28] we followed RHHS and used a corrected value only in one case (where $k = k_{solv} + k_{rear}$).[28] In other cases we did not attempt to use k_{ion} values for several reasons.

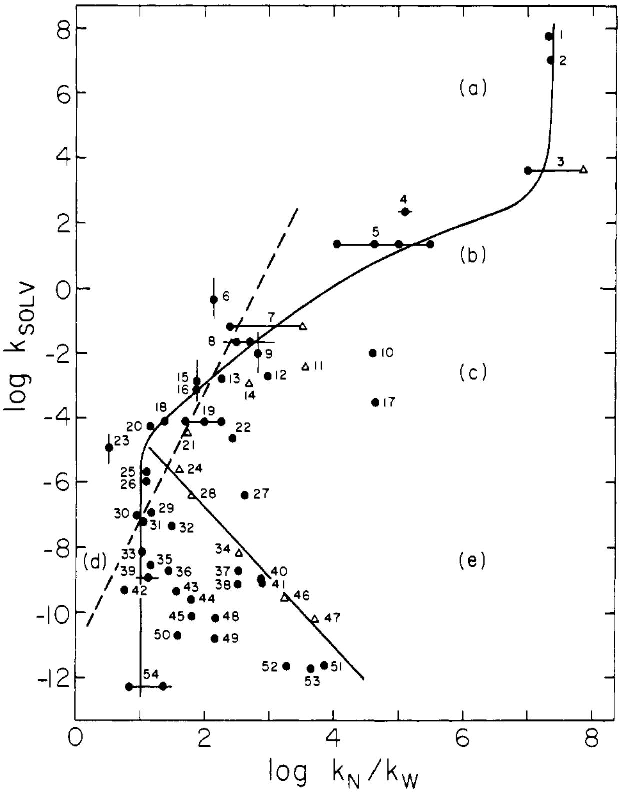

Figure 1. A plot of log k_{solv}(RCl) in 80% acetone at 25 °C vs. log (k_N/k_W). The numbers are those of Table III. Triangles are for Richard and Jencks' data,[25a] and circles for the other systems of Table III. Different reported values for the same system are connected by a line. A full line extending from a point reflects the calculated uncertainty. Mechanistic regions are designated by letters a–e. The dashed line is the RHHS line and the full line in region e is a regresion line through Richard and Jencks' S_N2 systems.

First, even when the extent of ion pair return can be estimated[28] the corrected value may still differ from k_{ion}, due to unmeasured hidden return. Second, such data are available only for a few compounds, and use of k_{ion} for several compounds and k_{solv} for others is unjustified. Moreover, k_{solv} values are almost always used for estimating carbenium ion stabilities. This seems to be justified since a linear correlation exists between log k_{solv}(RCl) values in EtOH and the heats of ionization of the same RCl to form R^+ in nonnucleophilic solvent mixtures.[29,30] However, a problem arises for compounds that solvolyze at least partially via a k_s process or via S_N2 reaction.

A second problem, previously discussed by RHHS,[11] is the ground-state effect when two different isomeric precursors RX and R′X give the same R^+ at different rates. This is the case for the allylic isomers PhCH(OPNB)CH=CHMe and PhCH=CHCH(OPNB)Me, which differ 300-fold in reactivity,[28b] but even the selectivities, which presumably should be identical, differ by a factor of 2.[32] The problem is less severe for the isomeric pairs $ArCH_2CHMeOTs$ and $MeCHArCH_2OTs$ (Ar = An, Tol, Ph)

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Table I. Dependence of k_N/k_W Values on $[H_2O]$ and Other Parameters in Aqueous Acetone

compd	$10^2[NaN_3]$, M	T, °C	% Me_2CO	k_N/k_W	ref
Ph_2CHBr	2	25	70	170	41
	4	25	90	200	41
	4	50	90	180	41
	4	25	70	100	14
	10	50	90	56[a]	20
Ph_2CHCl	50	50	66.7	96	14
	5	25	66.7	101[a]	39
	5	25	75	102,[a] 58,[b] 157[c]	39
	5	25	87.5	88,[a] 68[b]	39
	4-10[d]	35	80	50	42
	1	50	90	56[a]	20
Tol_2CHCl	5.2	0	50	1200,[e,f] 1606[a,g]	38a
	5.4	0	80	420,[e] 518[a]	38a
	5.1	0	85	316,[e] 401[a]	38a
	5.1	0	90	227,[e,h] 301[a]	38a
	5.1	10	90	316[e,i]	38b
	5	25	50	1112[a,j]	39
	5	25	66.7	888,[a] 577[b]	39
	5	25	75	716,[a] 503,[b] 579[c]	39
	5	25	87.5	400,[a] 291,[b] 384[k]	39
Ph_3CCl	0.1-0.2	25	94[l]	9×10^4	41
	0.15-0.3	−34	85	11×10^4	41
	4.7[m]	30	80	1.12×10^4	43
	5	25	66.7	365[a]	39
	5	25	75	556,[a] 2620[c]	39
	5	25	87.5	454,[a] 2420[k]	39
Ph_3CBr	*m*	30	80	4480	43
Ph_3CF	0.4	25	80	24×10^4	41
	0.13-0.25	25	50	28×10^4	41
Ph_3COAc	0.094[m]	30	80	4.48×10^4	43
Ph_3CSCN	0.1-0.2	25	50	3.1×10^5	41
6-(chloromethyl)benzo[*a*]pyrene	0.02	25	80	4.1×10^4 [n]	22
	0.1-0.5	25	50	3.9×10^4 [o]	22

[a] Calculated from $[\% RN_3]_\infty$ and corrected for N_3^- consumption by the reaction and by the liberated acid. [b] At $I = 0.30$ M with added $LiClO_4$ or $LiNO_3$. [c] In 75% dioxane. [d] Constant ionic strength $I = 1$ M. [e] Calculated from $[\% RN_3]_\infty$ and corrected for N_3^- consumption by the reaction. Comparison of $[\% RN_3]_0$ and $[\% RN_3]_\infty$ values suggest that correction as in footnote *a* is unnecessary. [f] $[\% RN_3]_\infty = 60\%$. [g] Minimum value since $[NaN_3]/[RCl] = 0.9$. [h] $[\% RN_3]_\infty = 60.3\%$. [i] $[\% RN_3]_\infty = 67\%$. [j] $[\% RN_3]_\infty = 50\%$. [k] In 87.5% dioxane. [l] Containing 2% dioxane. [m] Constant ionic strength $I = 0.094$ M. [n] From product composition; measured spectroscopically. [o] Measured kinetically from inhibition of the common ion effect.

where the rate ratios in the k_Δ route to form the same phenonium ions are 2–5.[33]

The main practical problem is to calculate k_{solv}(80% acetone, 25 °C) from literature data, which are frequently at different conditions. The necessary extrapolations related to temmperature, ionic strength, nucleofuge, or solvent determine the quality of the plot.

An example is the extrapolation required for a change in nucleofuge from *p*-nitrobenzoate (OPNB) to chloride. RHHS previously used a k_{Cl}/k_{OPNB} ratio of 3×10^4 in order to calculate k_{solv} for the allylic chloride **6** of Table III, presumably on the basis of data for the *tert*-butyl system,[34] for which we calculated a value of 2.64×10^4 at 25 °C in 80% acetone. Data for the Ph_2CHX system,[35] obtained by using the Grunwald–Winstein equation[36] and temperature extrapolation gave $k_{Cl}/k_{OPNB} = 4.41 \times 10^5$ in 80% acetone at 25 °C. This value may be more appropriate for use with the allylic systems whose k_{solv} is closer to that of Ph_2CHCl than for *t*-BuCl. However, this argument is based on the RSP, and we therefore gave both values in our table of revised values (Table III) and plotted them in Figure 1.

Temperature and solvent corrections were generally introduced by using the appropriate E_a values and Grunwald–Winstein *m* values[36] when available. Otherwise E_a values for closely related compounds or *m* values in closely related solvents were used. Corrections for the ionic strength effect were not necessary.

Problems in Calculation of Consistent k_N/k_W Values. Several problems are also associated with the calculations of reliable k_N/k_W values by using Scheme I. First, is free R^+ the only product-forming intermediate, or are there several cationoid intermediates with different or similar selectivities, giving an average overall selectivity? Second, is the assumption that the product-forming steps are first order in $[H_2O]$ and $[N_3^-]$ correct? Third, can incorrect k_N/k_W values result from product formation by nonsolvolytic routes? Fourth, can a general base catalysis by N_3^- in the water reaction affect the k_N/k_W values? Fifth, there are practical questions involving extrapolation dealing with solvent, temperature, nucleofuge, and ionic strength effects.

Dependence of the Selectivities on the Water Concentration. Scheme I implies a first-order dependence on H_2O in the $R^+ + H_2O$ step, i.e., the $[H_2O]$ terms appears in eq 1 when the dimensionless k_N/k_W values are calculated. The validity of this assumption is not encountered when selectivities of various R^+s are compared in the same media, e.g., water[5] or 50% TFE–50% H_2O,[25a] but it becomes pertinent on comparing data from various sources in different solvent compositions.

Water is always in a large excess over RX and the possibility of a solvent sorting in the vicinity of the transition state cannot be discarded. In this case, if a large fraction of the ROH derives from collapse of the solvent shell, the k_N/k_W values will be little affected by a change in the water concentration. In studies in the binary mixtures H_2O–EtOH,[9] EtOH–TFE,[37] and TFE–H_2O[37b] it was assumed that each of the solvent components reacts with

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R^+ in an overall second-order process, and equations similar to eq 1 were used for calculating the selectivities. The assumption may be justified since both solvents compete for a position in the immediate solvation shell around R^+. This is not the case of N_3^- vs. H_2O competition.

The relevant data, which are available only for four systems (Table I), do not give a clear-cut answer. One view is due to Ingold et al. whose solvolysis of (p-$MeC_6H_4)_2CHCl$ in 50–90% acetone at 0 °C involves the most extensive change in solvent composition.[38a] They found that the final $[RN_3]$ values ($[RN_3]_\infty$) were independent of $[H_2O]$. The relevant k_N/k_W values, calculated by us, change accordingly from 227 in 90% acetone to 1200 in 50% acetone. Golomb's[39] results also show dependence of the dimensionless k_N/k_W on $[H_2O]$ for the same system in 50–87.5% acetone. As stated by Ingold in 1969 "provided sufficient water is present for the purpose, the first formed carbonium ion is solvated by a shell of fixed composition so that the rates at which the ion covalently unites with one of the solvating water molecules is independent of the composition of the bulk of the medium".[8a] Supporting evidence is the constancy of the $\alpha_{Cl} = k_{Cl}/k_{H_2O}[H_2O]$ (M^{-1}) values for $C_6H_5CH(Cl)C_6H_4X$-p (X = t-Bu, H) in 80% and 90% acetone and for (p-$MeC_6H_4)_2CHCl$ in 70% and 90% acetone.[20] Likewise, reduction of Ph_2CHCl or $PhCMe_2Cl$(RCl) by BH_4^- under solvolytic conditions gives a solvent-independent percentage of the reduction products (RH) in 65–88% diglyme.[40]

The other data of Table I are consistent with a first-order dependence on $[H_2O]$. Five different groups investigated the benzhydryl system,[14,20,39,41,42] and Table I shows that the k_N/k_W values for the bromide in 70–90% acetone and for the chloride in 66.7–87.5% acetone that are obtained in the same laboratory are nearly independent of the solvent composition. Likewise, the k_N/k_W values for the chloride and the bromide in media of similar compositions are similar when measured in the same laboratory, but they differ if measured in two laboratories.

For the trityl (Ph_3CX) system Swain and co-workers[41] found reasonably $[H_2O]$-independent k_N/k_W values for X = Cl, F. However, the values were nucleofuge dependent, being in a 1:2.6:3.1 ratio for X = Cl, F, SCN, respectively. Nearly constant dimensionless k_N/k_W values for X = Cl result also from Golomb's data[39] but they were 200-fold lower than those of Swain.[41] Both the lower values and the dependence on the nucleofuge were ascribed by Hill[43] to insufficient mixing during the reaction, resulting in a local depletion of N_3^- in the vicinity of the rapidly generated ion. Indeed, by applying rapid mixing, his values for X = Cl are 20-times larger than those of Golomb. The relative k_N/k_W values also increased when formation of R^+ was slower, being 1:2.5:10 for X = Br, Cl, OAc, respectively.

Mild support for solvent-independent k_N/k_W values comes from the decrease of the α_{Cl} values for Ph_2CCl_2 on increasing the water content in 70–85% acetone.[21b] Similar behavior was observed in solvolysis of vinyl bromides in TFE–H_2O.[44]

k_W was measured directly only twice in two solvent compositions. In the reaction of the (p-(dimethylamino)phenyl)diphenylcyclopropenium ion with water in 20% MeCN–80% H_2O and in 2% MeCN–98% H_2O, Green and Taft[45a] found $k_W[H_2O]$ values of 0.22 and 0.34 s^{-1}, respectively, giving the relatively $[H_2O]$-independent 10^3k_W values of 4.95 and 6.24 M^{-1} s^{-1}. However, for 9-arylxanthydrol (Ar = Ph, p-An) the same k_W-$[H_2O]$ values were found in 20% MeCN–80% H_2O and in dilute aqueous $HClO_4$.[45]

Table II. Concentration Dependence of the k_N/k_W Values

compd	solvent	T, °C	$[NaN_3]$, M	k_N/k_W
1-adamantyl bromide	75% dioxane[11]	100	0.06	20
			0.10	8.9
	80% EtOH[11]	75	0.02	5.5^a
			0.04	2.5^a
			0.06	2.5^a
	67% EtOH[14]	77	0.01	233^b
			0.05	11^b
			0.5	2.7^b
2-adamantyl tosylate	75% dioxane[11]	75	0.06	32
			0.10	16
	80% EtOH[11]		0.02	0.82^a
			0.04	1.7^a
			0.06	2.0^a
Ph_3CCl[43]	80% acetone	30	0.0056	256
			0.047	11120
p-TolCH(Ph)-OPNB[46]	90% acetone	99.5	0.03	185
			0.0655	191
			0.116^c	123
p-AnCH(Me)-OPNB[47]	90% acetone	78.6	0.030^d	241
			0.050^d	260
			0.078^d	239
			$0.106^{d,e}$	238
			0.125^d	217
			0.153^d	192
			0.202^d	176
c-C_5H_9OMs[14]	67% diglyme	40	0.05	632
			0.5	242

[a] Based on very low percent RN_3 (0.1–0.7%). [b] k_N/k_{SOH} values, probably calculated from ([% RN_3]/([% ROH] + [% ROEt]))[([H_2O] + [EtOH])/[NaN_3]]. [c] The solubility of NaN_3 above this concentration is limited. [d] Reaction with Bu_4NN_3. [e] See text.

Consequently, no definite conclusion concerning the dependence of the k_N/k_W values on the $[H_2O]$ term is presently possible, and we therefore, in cases of doubt, gave a range of dimensionless k_N/k_W values on the basis of the available data and the assumptions used for deriving eq 1.

Dependence of the k_N/k_W Values on the N_3^- Concentration. Equation 1 is also based on the assumed first-order dependence on the $[N_3^-]$ term in the capture process. Indeed, k_N/k_W values that are independent of the $[N_3^-]$ were found for the relatively reactive Ph_2CHCl,[41] p-Tol_2CHCl,[38a] Ph_3CCl,[41] and PhCH(OPNB)CH=CHMe.[32] With other, mostly less reactive systems, the k_N/k_W values decrease appreciably on increasing $[NaN_3]$ in aqueous EtOH, acetone, and dioxane, as shown in Table II.

In several cases a 2-fold decrease in $[NaN_3]$ results in a ca. 2-fold increase in k_N/k_W, and for 1-adamantyl bromide in 67% ethanol k_N/k_W decreases 21-fold on a 5-fold increase in $[NaN_3]$.[14] An explanation that was previously used[26,48] for interpreting the behavior of "borderline" substrates[49] is ion pairing of NaN_3 at the concentration used. Incomplete dissociation of the $Na^+N_3^-$ ion pair to free N_3^- and lower reactivity of the ion-paired N_3^- toward the cation will account for the increased selectivity. This is probably the explanation for the behavior of p-TolCH(Ph)-OPNB.[46] The "true" k_N/k_W values should then be obtained either by using N_3^- activities or by extrapolating the k_N/k_W to $[NaN_3]_0$. These procedures were not applied when necessary, and the literature values are at different NaN_3 concentrations. The problem is more important for less-reactive substrates, when the k_N/k_W values are relatively low, and higher NaN_3 concentrations are required for observing the RN_3.

Another explanation is ion pairing of the cationoid species. In the solvolysis of dianisylmethyl mesitoate in MeOH at a constant ionic strength,[50] the selectivity parameter (% RN_3)/((%

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ROMe)[N_3^-]) decreased from 1850 at 10^{-5} M NaN_3 to 950 at 10^{-3} M NaN_3. At these concentrations ion pairing of $Na^+N_3^-$ is relatively unimportant. Ritchie suggested that "at least two intermediates with different selectivities are being trapped by N_3^-...." and concluded that "it is clear that the ion pair is considerably less selective".[50] The decrease of the k_N/k_W values for *p*-AnCH(Me)OPNB with Bu_4NN_3 in 90% acetone[47] when [N_3^-] > 0.106 M can be explained similarly. This is augmented by the observed change from a special salt effect at lower [N_3^-] to a normal salt effect at higher ones.[47]

If ion pairs are important in determining the selectivities of highly reactive RCl, their importance should be higher for less reactive substrates. Indeed, *p*-chlorobenzhydryl *p*-nitrobenzoate reacts with N_3^- in 90% acetone[28a] exclusively at the ion pair stage so that free ions are probably not involved in reactions of less reactive substrates such as 1- and 2-adamantyl halides. Consequently, different cationoid species are probably captured at the two ends of the RHHS plot. However, an ion pair is not necessarily less selective than a free ion. Ritchie found very similar selectivities of a free triarylmethyl cation and an analogous zwitterionic model,[51] and Sunko[14] suggested that an intimate ion pair is more selective than more dissociated species.

Other differences between the stoichiometric and the actual N_3^- concentration are local depletion of N_3^- in an insufficiently mixed solution and consumption of N_3^- during the reaction by formation of RN_3 and by its reaction with the acid formed. This is important since in many of the reported studies [NaN_3] ~ [RCl] and in most cases only [RN_3]$_\infty$ values are measured.

Corrections for N_3^- consumption were introduced previously, but not systematically. Swain[41] and RHHS[11] took into account N_3^- consumption due to the reaction, while Sneen[10] corrected also for N_3^- consumption by the formed acid. Sneen's values seem sometimes to be overcorrected: e.g., in the solvolysis of PhCH(OPNB)CH=CHMe[32a] his value is 220[10] while our calculated value is 140. In this case [N_3^-]/[RCl] > 9 and the pK_a's of HN_3 (4.68 in H_2O)[52a] and of 4-$O_2NC_6H_4COOH$ (3.41 in H_2O)[52b] may be similar in the solvent used.

Temperature and Ionic Strength Effects on the Selectivity. The competitive capture of R^+ by the ion N_3^- and the neutral H_2O should be sensitive to the ionic strength (*I*). A change in *I* could also affect the selectivity by changing the relative concentration of the product-forming cationoid species.[14] A temperature effect is expected if the E_a's of the capture processes differ significantly.

Ingold et al. found that $E_a(N_3^-) - E_a(H_2O) = 4$ kcal·mol^{-1} for Tol_2CHCl in 90% acetone,[38b] and Bunton et al.[53] found $E_a(N_3^-) - E_a(MeOH) = 2$–3 kcal·mol^{-1} for the reaction of camphene hydrochloride in MeOH/NaN_3, i.e., the selectivities increased with the temperature. Ingold[38b] developed an equation that calls for a strong decrease of the k_N/k_W value at very low [N_3^-] on increasing *I* and depending on the dielectric constant ϵ. According to this equation the k_N/k_W value at 0.05–0.2 M NaN_3 in 90% acetone can be 2–3 times smaller than the value extrapolated to $I = 0$. Indeed, Golomb[39] found that the formation of RN_3 from $(p\text{-}XC_6H_4)_2CHCl$ (X = H, Me) in 66.7–87.5% acetone decreased 1.3–1.75 times on increasing *I* from 0.05 to 0.3. However, Ingold et al.[38a] did not find a strong effect of *I* on the α_{N_3} for Tol_2CHCl, which was independent of ϵ in 50–90% acetone or of *I* at 0.05–0.2 M NaN_3 in 50% acetone. Likewise, a similar selectivity was obtained for Ph_2CHBr at 25 °C and at 50 °C in the same solvent at the same *I* value,[41] and the k_N/k_W value is the same for Ph_2CHCl at 50 °C and $I \sim 0.5$ and Ph_2CHBr at 25 °C and $I = 0.04$[14] (Table II). Consequently, there is no experimental evidence for a strong effect of the temperature or *I* on the k_N/k_W values, and the error introduced in the RS plots by the use of k_N/k_W values measured at moderately different *I* or t^0 values is small.

Solvent Effect. Increase in ϵ should decrease k_N more than k_W,[54] and may change the relative distribution of the cationoid intermediates and hence the overall selectivity. The EtOH vs. H_2O selectivities (k_E/k_W) for Ar_2CHCl change linearly with *Y* in 70–95% aqueous EtOH,[9f] but they are solvent independent for *exo*-norbornyl and the 1- and 2-adamantyl systems.[9b] However, the k_N/k_W values for 1-adamantyl bromide and 2-adamantyl tosylate are higher at 75% dioxane than in 80% EtOH.[11]

In spite of the above prediction, both α_{N_3} and α_{Cl} for the benzhydryl system are independent of the solvent composition in aqueous acetone.[20,38] A change from aqueous acetone to aqueous dioxane at the same [H_2O] reduced RN_3 production from Tol_2CHCl but enhanced it from Ph_2CHCl[39] (Table I). Swain[41] obtained k_N/k_W values for Ph_3CX and Ph_2CHBr that are independent of ϵ (Table I) as is the case for the k_{Cl}/k_W values of Ph_2CCl_2 in aqueous acetone.[21b] In contrast, the dimensionless k_{Br}/k_{SOH} ratios for the solvolysis of AnC(Br)=CMe_2 in TFE–H_2O decreased on increasing [H_2O].[44] The small decrease of k_N/k_W on increasing *Y* for *p*-$XC_6H_4CH(CMe_3)OMs$, X = H, Me, *t*-Bu, Br, in aqueous acetone was ascribed to an S_N2 process.[55]

In previous RS plots k_N/k_W values in different solvent systems such as 60% dioxane,[32a] 67% aqueous diglyme,[56] and 80% EtOH[11] were used. In Table III we mostly ignored possible differences in the values in various aqueous solvents, but solvent corrections were sometimes necessary. Compounds ArCH=CHCH(OPNB)Me (Ar = *p*-Tol, Ph)[32] and $An_2CHOCOC_6H_2Me_3$-2,4,6[50] were studied in MeOH/N_3^-, and we obtained k_N/k_W values by using the factor $k_{MeOH}[MeOH]/k_W = 93$, which we found for PhCH(OPNB)CH=CHMe.[32a] The k_N/k_W for *p*-$Me_2NC_6H_4CH(Me)OAc$[57] was calculated from k_N/k_{EtOH} by using $k_E/k_W = 6$ as found for compound **12** of Table III.[57] In calculating k_N/k_W for compounds ArCH(X)Me from the given k_N/k_{SOH}[SOH] values in 50% aqueous TFE,[25a] we used the appropriate k_W/k_{TFE} ratios.[58a]

Nucleofuge Effect. For a product formation from free ions the selectivity should be independent of the nucleofuge (leaving group). However, if ion pairs are involved in product formation, i.e., when k_{solv} is low,[26] the overall selectivity should reflect their distribution and selectivities that are nucleofuge dependent.[59]

For example, studies on optically active and oxygen-labeled *p*-$ClC_6H_4CH(Ph)OPNB$ suggested that N_3^- captures completely a solvent-separated ion pair.[28a] In contrast, N_3^- does not capture completely the intermediate(s) involved in the racemization of *p*-$ClC_6H_4CH(Ph)Cl$.[27b] For the more reactive Ph_2CHX system the selectivities are identical for X = Cl, Br.[14,20] With the very reactive Ph_3CX system the increase in the k_N/k_W values in the order X = SCN > F > AcO > Cl > Br, was attributed to a local depletion of [N_3^-] near R^+ and not to ion pairing.[43] With esters as nucleofuges, N_3^- may give acyl oxygen cleavage by attack on

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(59) Somewhat surprisingly the small differences between the k_E/k_W values for the $PhCH_2X$ and 2-$C_8H_{17}X$ systems, X = Cl, Br, OTs, were ascribed to a reaction via the solvent-separated ion pairs.[9g]

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Table III. Solvolysis Rates and k_N/k_W Values for Alkyl Chlorides (RCl) in 80% Acetone at 25 °C

no.	substrate	k_{solv}, s^{-1}	k_N/k_W	log k_{solv}	log (k_N/k_W)
1	p-$O_2NC_6H_4N_2^+$	5.7×10^{7} [a]	2.04×10^{7} [b,90]	7.75	7.31
2	(p-An)$_3$CCl	1.05×10^{7} [a]	2.3×10^{7} [19c]	7.02	7.36
3	p-$Me_2NC_6H_4CH(Me)Cl$	3.85×10^{3} [c]	7.3×10^{7} [d,58b] 1.0×10^{7} [e]	3.59	7.87, 7.0
4	p-An_2CHCl	214[f]	$(0.9\text{–}1.7) \times 10^{5}$ [g]	2.33	5.0–5.2
5	Ph_3CCl	21.9[h,62]	11 200,[i] 44 800[j] 10^{5},[k] 3.1×10^{5} [l]	1.34	4.05, 4.65; 5, 5.49
6	PhCH(Cl)CH=CHCH$_3$	0.12–2.0[m,n]	140[o]	−0.92 to −0.30	2.15
7	p-AnCH(Me)Cl	6.54×10^{-2} [60]	243,[p] 3300[d]	−1.18	2.40, 3.52
8	p-Tol_2CHCl	2.2×10^{-2} [q]	227–1200,[r] 400–1110[s]	−1.65	2.36–3.08, 2.3–2.75
9	p-TolCH=CHCH(Me)Cl	$(2.5\text{–}41) \times 10^{-3}$ [m]	670 ± 100[t]	−2.6 to −1.4	2.83 ± 0.06
10	6-(chloromethyl)benzo[*a*]pyrene	9.4×10^{-3} [22]	4.0×10^{4} [u]	−2.03	4.60
11	p-$CH_3SC_6H_4CH(Me)Cl$	3.37×10^{-3} [60]	3600[d]	−2.47	3.56
12	3-benzothienyl-CH(Me)Cl	1.89×10^{-3} [v]	950[w]	−2.72	2.98
13	p-TolCH(Ph)Cl	1.57×10^{-3} [63]	188[x]	−2.80	2.27
14	p-$PhOC_6H_4CH(Me)Cl$	1.15×10^{-3} [64]	510[d]	−2.94	2.71
15	PhCH=CHCH(Me)Cl	$(3.5\text{–}59) \times 10^{-4}$ [m]	75[y]	−3.5 to −2.2	1.88
16	p-t-$BuC_6H_4CH(Ph)Cl$	7.6×10^{-4} [z]	74[aa]	−3.12	1.87
17	9-(chloromethyl)anthracene	2.96×10^{-4} [22]	4.5×10^{4} [ab]	−3.53	4.65
18	1-Me-c-C_5H_9Cl	7.8×10^{-5} [ac]	24[ad]	−4.11	1.38
19	Ph_2CHCl	7.27×10^{-5} [65]	50,[42] 56,[ae] 100,[af] 180[ag]	−4.14	1.7, 1.75, 2.0, 2.26
20	p-$CH_3OC_6H_4CH_2Cl$	5.7×10^{-5} [ah,aj]	14.9[ai,aj]	−4.24	1.17
21	p-TolCH(Me)Cl	3.47×10^{-5} [64]	52[d]	−4.46	1.72
22	p-$ClC_6H_4CH(Ph)Cl$	2.31×10^{-5} [ak,27b]	280[al]	−4.64	2.45
23	2-Me-2-adamantyl-Cl	$(3.7\text{–}29) \times 10^{-6}$ [am]	3.3[an]	−5.4 to −4.5	0.52
24	p-$FC_6H_4CH(Me)Cl$	2.43×10^{-6} [c]	44[d]	−5.61	1.65
25	Me_3CCl	1.97×10^{-6} [34a]	12[ao]	−5.71	1.08
26	1-Me-c-$C_3H_4CH_2Cl$	1.11×10^{-6} [ap]	12[aq]	−5.95	1.08
27	p-$PhOC_6H_4CH_2Cl$	4.06×10^{-7} [aj,ar]	415[ai,aj]	−6.39	2.62
28	m-AnCH(Me)Cl	3.82×10^{-7} [69]	64[d]	−6.41	1.81
29	1-Me-c-C_4H_6Cl	1.15×10^{-7} [ap]	15[aq]	−6.94	1.18
30	p-TolCH(CMe$_3$)Cl	1.06×10^{-7} [77]	8.8[as]	−6.97	0.94
31	p-t-$BuC_6H_4CH(CMe_3)Cl$	6.11×10^{-8} [77]	11.3[as]	−7.21	1.05
32	c-$C_3H_5CH_2Cl$	4.81×10^{-8} [ap]	31[aq]	−7.32	1.49
33	*exo*-norbornyl-Cl	7×10^{-9} [ap]	11[at]	−8.15	1.04
34	m-$BrC_6H_4CH(Me)Cl$	6.4×10^{-9} [60]	335[d]	−8.19	2.53
35	PhCH(CMe$_3$)Cl	2.8×10^{-9} [77]	14.4[as]	−8.55	1.16
36	c-C_4H_7Cl	1.81×10^{-9} [ap]	28[aq]	−8.74	1.45
37	p-$AnCH_2CH(CH_3)Cl$	1.73×10^{-9} [au]	348[33]	−8.76	2.54
38	$CH_3CH(p\text{-}An)CH_2Cl$	7.8×10^{-10} [au]	348[av]	−9.11	2.54
39	1-adamantyl-Cl	1.2×10^{-9} [aw]	9–20[ax]	−8.92	0.95–1.30
40	Me_2CHCl	1.05×10^{-9} [ay,33]	740[ay,33]	−8.98	2.87
41	n-$C_6H_{13}CH(Me)Cl$	9.56×10^{-10} [ay,33]	770[ay,33]	−9.02	2.89
42	c-$C_8H_{15}Cl$	5×10^{-10} [az]	<6[ba]	−9.3	<0.78
43	p-$BrC_6H_4CH(CMe_3)Cl$	4.6×10^{-10} [bb]	39.2[as]	−9.34	1.59
44	p-$TolCH_2CH(CH_3)Cl$	2.6×10^{-10} [au]	61[33]	−9.59	1.79
45	$CH_3CH(p\text{-}Tol)CH_2Cl$	7×10^{-11} [au]	61[av]	−10.15	1.79
46	p-$NCC_6H_4CH(CH_3)Cl$	2.79×10^{-10} [c]	1730[d]	−9.55	3.24
47	p-$O_2NC_6H_4CH(CH_3)Cl$	6.15×10^{-11} [c]	5300[d]	−10.21	3.73
48	$PhCH_2CH(CH_3)Cl$	6.8×10^{-11} [au]	148[33]	−10.17	2.17
49	$CH_3CH(Ph)CH_2Cl$	1.47×10^{-11} [au]	148[av]	−10.83	2.17
50	*endo*-norbornyl-Cl	2×10^{-11} [bc]	39[at]	−10.70	1.59
51	$CH_3CH(p\text{-}An)CH_2Cl$	2.34×10^{-12} [bd,33]	7400[be,33]	−11.63	3.87
52	$CH_3CH(p\text{-}Tol)CH_2Cl$	2.17×10^{-12} [bd,33]	1870[be,33]	−11.66	3.27
53	$CH_3CH(Ph)CH_2Cl$	1.99×10^{-12} [bd,33]	4500[be,33]	−11.70	3.65
54	2-adamantyl-Cl	5.3×10^{-13} [ap]	6.6,[bf] 16–32[bg]	−12.28	0.82, 1.2–1.51

[a] For calculation see text. [b] A lower limit since reaction with N_3^- may not be rate determining. [c] Calculated by using the equation log $(k/k_0) = -4.953(\sigma_p^{\circ} + 1.147(\sigma_p^{+} - \sigma_p^{\circ}))$ at 45 °C and corrected to 25 °C by multiplying by 1.04.[60] [d] Calculated from the k_N/k_{SOH}[SOH] values of ref 25a (see text). $I = 0.5$ at room temperature; nucleofuges, 3,5-$Cl_2C_6H_3S^-$ for compound 3, $RC_6H_4COO^-$ for compounds 7, 11, and 14, and Cl for compounds **21**, **24**, **28**, **34**, **46**, and 47. [e] Estimated lower limit from the solvolysis of p-$Me_2NC_6H_4CHMeOAc$ in EtOH/0.002 M NaN_3 that produces no acid up to 90% N_3^- consumption,[57] assuming that 5% acid could have been detected and corrected for the different solvent. [f] Calculated from data at 0 °C in 85% acetone.[61] Temperature and solvent corrections were introduced by comparing the ρ^+ values for compounds 13, 16, 19, and **22** in 85% acetone at 0 °C and in 80% acetone at 25 °C.[20,27b,61,63,65] The previously reported $k_{solv} = 27$ s^{-1} [2a] was based on less data. [g] A calculated lower limit from the $[RN_3]/([ROH][N_3^-])$ values of 1850–950 for $An_2CHOCOC_6H_2Me_3$-2,4,6 in MeOH,[50] assuming that $k_{MeOH}[MeOH]/k_W = 93$ as found for compound **6**. [h] A directly measured value in a flow system. The previously quoted k_{solv} value is 8.8 (8.9) s^{-1} [2a,11,22] (see text). [i] Calculated from α_{N_3} for Ph_3CCl in ref 43. The previously reported value of 1000[11] is $\alpha_{N_3} = k_N/k_W[H_2O]$. [j] Calculated for Ph_3COAc.[43] [k] An average value for Ph_3CCl from ref 41. [l] For Ph_3CSCN.[41] [m] From the data for ROPNB in 60–80% dioxane[28b] and using k_{Cl}/k_{OPNB} ratios of 2.6×10^4 and 4.4×10^5 (see text). [n] $k = k_{solv} + k_{rearrangement}$.[28b] [o] Calculated average value from data for ROPNB in 60% dioxane/0.15–0.45 M NaN_3.[32a] [p] Calculated for ROPNB in 90% acetone/0.03–0.106 M Bu_4NN_3 at 78.6 °C[47] (cf. Table II and text). A value of 470 in 50% acetone at 25 °C, $I = 0.5$ was recently found (Jencks, W. P., personal communication). [q] Calculated from ref 20, assuming that $E_a = 17$ kcal·mol^{-1}, a value extrapolated from systems 13 and 19.[63] [r] In 50–90% acetone[38] (Table I). The reported values were 180[11] and 875[10] (see text). [s] In 50–87% acetone[39] (Table I). [t] From data in MeOH (see text). [u] An average value (see Table I). [v] Calculated from k_{solv} of compound 14,[64] assuming that $[k_{solv}(12\text{-OAc})/k_{solv}(14\text{-OAc})]$ (30% EtOH)[57] = $[k_{solv}(\mathbf{12}\text{-Cl})/k_{solv}(\mathbf{14}\text{-Cl})]$ (80% acetone). [w] Calculated from $[ROH]_\infty$ and $[RN_3]_\infty$ in the reaction of ROAc in 30% EtOH/0.035 M NaN_3 at 75 °C.[57] [x] Calculated from data for ROPNB in 90% acetone/0.030–0.065 M NaN_3 at 99.5 °C.[46] [y] Calculat-

Footnotes to Table III (*Continued*)

ed from data for $ROOC_6H_3Cl_2$-2,6 in MeOH.[32b] For solvent extrapolation see text. [z] An average value from ref 20. The reported value[11] is 4.77×10^{-4} s^{-1} from ref 66 in the presence of 0.1 M NaCl. [aa] Calculated from the initial $[RN_3]/[ROH]$ ratio in 90% acetone at 50 °C.[66] [ab] Determined by an indirect kinetic method in 50% acetone/0.0005–0.003 M NaN_3.[22] [ac] Calculated from $k_{solv} = 3.67 \times 10^{-4}$ s^{-1} in 80% EtOH at 25 °C[67] assuming $m = 1$. [ad] In 67% aqueous diglyme.[14] [ae] From ref 20 (see Table I). Previously quoted values are 34[11] and 61.[10] [af] Average value from ref 14 and 39 (Table I). [ag] Average value for Ph_2CHBr[41] (Table I). [ah] Based on k_{solv} at 20 °C[68] using $E_a = 21$ kcal·mol^{-1} as for Ph_2CHCl.[63] [ai] Value from ref 69. The reaction with N_3^- is probably S_N2.[68,70] [aj] Values for compounds 20 and 27 were erroneously exchanged in ref 69 and 70. The correct assignment is given in ref 68 and 71. [ak] The polarimetric rate constant k_α is 6×10^{-5} s^{-1}. [al] Calculated from data for p-$ClC_6H_4CH(OPNB)Ph$ with 0.14 M NaN_3 at 100 °C and corrected for the acyl oxygen cleavage by the N_3^- (see text). [am] (i) By using k_{solv} for ROPNB[72] and $k_{Cl}/k_{OPNB} = 2.6 \times 10^4$ [34] $k_{solv} = 3.7 \times 10^{-6}$ s^{-1}; (ii) by using k_{solv} for 2-adamantyl-Cl and a k_{Me}/k_H ratio of 10^7 [74] (interpolated from ratios in 80% EtOH and AcOH),[73] $k_{solv} = 29 \times 10^{-6}$ s^{-1}; (iii) from $k_{solv} = 1.05 \times 10^{-2}$ s^{-1} for 2-methyl-2-adamantyl-Cl in 80% EtOH at 70 °C and $\Delta H^\ddagger = 22.3$ kcal·mol^{-1} [74] assuming that $m = 1.0$, $k_{solv} = 14 \times 10^{-8}$ s^{-1}. [an] In 70% acetone.[14] [ao] For t-BuBr. For previous values see text. [ap] Calculated in ref 11. [aq] For ROMS in 67% diglyme–0.5 M NaN_3 at 40 °C.[56] [ar] Calculated from $k_{solv} = 1.63 \times 10^{-6}$ s^{-1} in 70% acetone at 20 °C,[68] using $m = 1.08$ as for compound 20,[68] and an $E_a = 21$ kcal·mol^{-1} as for Ph_2CHCl.[63] [as] Data for ROMs at 35 °C in 80% acetone. The k_N/k_W values at 7 °C for compounds 30 and 31 are 9.4 and 12, respectively. The reaction with N_3^- was defined as S_N2.[55] [at] Value for ROTs[78] at unspecified solvent and temperature. [au] $k_{solv} = k_\Delta$ for the formation of the phenonium ion, calculated from ref 33 and assuming that k_Δ/k_s (RCl, 80% acetone) = k_Δ/k_s (ROTs, 80% EtOH). [av] Values measured for the isomeric system that gives the same carbenium ion. [aw] Estimated in ref 79 from data in aqueous EtOH and aqueous acetone. [ax] Data for the bromide in 75% dioxane. Previously reported value is 2.5[11] (see text). [ay] Reaction with water follows the k_s route. Reaction with N_3^- is S_N2.[9e,33] [az] Estimated from $k_{solv} = 3.19 \times 10^{-5}$ s^{-1} in 80% EtOH for the 1-methyl derivative,[80] using k_{Me}/k_H ratio of 25 000 (average of the ratio for c-C_5H_9OTs in 80% EtOH at 85 °C and c-$C_6H_{11}Cl$ in 50% EtOH at 95 °C)[81] and $m = 0.67$ as for ROTs in aqueous EtOH.[82] [ba] Based on the formation of <1% RN_3 from cyclooctyl-OTs in 70% EtOH/0.04 M NaN_3[82] and on $k_E/k_W = 0.62$ for c-$C_8H_{15}OBs$.[83] [bb] Calculated from data for ROMs using a k_{OMs}/k_{Cl} ratio of 4200 (average value for systems 30, 31, and 35).[77] [bc] Calculated by using $k_{exo}/k_{endo} \sim 400$ in 80% acetone (based on extrapolated data from ref 84). [bd] $k_{solv} = k_s$. [be] For ROTs in 80% EtOH. The reaction with N_3^- is probably S_N2.[33] [bf] Value for ROTs in 70% acetone.[14] [bg] Calculated for ROTs from data in 75% dioxane[11] (cf. Table II). For the previously reported value, see text.

the carbonyl group. Hydrolysis of the acyl azide formed will increase k_W and reduce the calculated k_N/k_W value, as indeed happened for p-$ClC_6H_4CH(Ph)OPNB$.[28a]

Unfortunately, the literature k_N/k_W values were mostly determined with a single nucleofuge, which was chloride only in the minority of the cases. This should affect the quality of the RS plot.

Extended log k_{solv} vs. k_N/k_W Table. Differences from Previous Tables. Table III gives log k_{solv} and k_N/k_W values for 54 compounds. The data are plotted in Figure 1. Several differences distinguish Table III from Sneen's[10] and RHHS'[11] tables.

It is much more extensive since Sneen[10] used 7 compounds, RHHS used 16 compounds[11] in their correlations, and we introduced all the relevant new data known to us. Especially important are Richard and Jencks' recent data on ArCH(X)Me derivatives of wide structural range[25] where the S_N1–S_N2 borders are sharply defined by the kinetics. We also included two stable ions in order to evaluate the shape of the line in Ritchie's region and β-arylalkyl systems that react via the k_Δ route.[33] For defining the S_N2 region we included ArCH(Cl)Me derivatives with electron-withdrawing aryl groups,[25b] benzyl derivatives, $ArCHMeCH_2OTs$, i-PrCl, and 2-$C_8H_{17}Cl$, which probably react via S_N2 with N_3^- and via the k_s route with water.[25b,33,68,70] We checked all the literature data and the assumptions involved in the calculation of the k_{solv} and k_N/k_W values, and the data were mostly recalculated. Although it is not meant as a criticism[86] the reasons for the discrepancy between previous and present values are of interest. They are discussed above and in footnotes to Table III, and a few typical cases are analyzed briefly below.

Two compounds from the RHHS plot[11] were omitted: γ-methyl-α-p-tolylallyl chloride, where the selectivity of the allylic isomer was measured, and α,α-dimethylallyl chloride, for which added NaN_3 appreciably increased k_{solv}; the k_N/k_W values decrease from 325 at 0.04 N NaN_3 to 80 at 0.5 M NaN_3,[32b] and the reaction with N_3^- is complex.[32b]

Ph_3CCl was the most reactive compound on the previous RS plots, and its position largely determined their shape near the intersection with Ritchie's region. The previous k_{solv}[2a,11,22] was extrapolated from 85% acetone at −34 and −14 °C but we used instead a directly measured value in 80% acetone at 25 °C.[62] RHHS's k_N/k_W value of 1000[11] is apparently Hill's α_N value[43] and should be multiplied by 11.2, the water concentration in 80% acetone. We discussed above the problems that led to multiplicity of k_N/k_W values for Ph_3C^+. In the absence of an objective judgement as to the best value, we included all of them in Table III and drew a line in Figure 1.

The previously reported $k_{solv} = 0.134$ s^{-1} for the γ-methyl-α-phenylallyl system is based on k_{solv} for the p-nitrobenzoate[28b] and a k_{Cl}/k_{OPNB} of 3×10^4. For PhCH(Cl)CH=CHMe Sneen gave the relative ratio $k_{solv}(RCl)/k_{solv}(t\text{-}BuCl) = 940$ at 0 °C.[10] However, if $E_a = 21.6$ kcal·mol^{-1} in 80% acetone as in 70% dioxane[28b] and $k_{Cl}/k_{OPNB} = 8.3 \times 10^4$ in 80% acetone at 0 °C,[34] we can calculate $k_{solv}(RCl)/k_{solv}(t\text{-}BuCl)$ ratio of 306 000. We cannot account for the difference unless k_{solv} for the ~300 times slower isomer, PhCH=CHCH(OPNB)Me, was mistakenly used.

Our k_N/k_W values for Tol_2CHCl differ from earlier values: First, since the $[RN_3]_\infty/[ROH]_\infty$ ratios are $[H_2O]$ independent,[38a] we gave a range of k_N/k_W values covering all the solvent compositions, while Sneen[10] used only the data at 50% acetone. Second, the RHHS value is the only one that was massively corrected for the ionic strength and temperature effect,[38b] but we see no necessity for such a correction. Third, the $[H_2O]$ term of 5.5 M in 90% acetone was apparently previously forgotten.[11]

For p-$ClC_6H_4CH(OPNB)Ph$[87] a k_N/k_W value of 56 was calculated by RHHS.[11] However, the percent RN_3 was calculated from the difference between the calculated and observed titratable acid at 100% reaction, and since 82% of the acid arises from acyl oxygen cleavage of the ester,[28a] the k_N/k_W value corrected for this and for N_3^- consumption is 280.

All the selectivity values for t-BuCl are based on Ingold's data for t-BuBr in 90% acetone.[75] From the given percentages of the total reaction and the acid formed,[75] we calculated a time-averaged k_N/k_W value of 7 ± 1. However, the solvolysis of t-BuBr in 90% acetone is accompanied by 38% acid-generating elimination.[76]

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Correcting for this we obtained $k_N/k_W = 12$. The values reported by Sneen (14.5),[10] RHHS (74),[11] and Swain (3.9)[41] suggest that Swain used only the $[RN_3]_\infty$ value, that Sneen overcorrected for the N_3^- consumption by the acid, and that the RHHS value reflects a typographical error.[88]

For the 1-adamantyl system the RHHS value of 2.5 is apparently based on data for the bromide in 80% EtOH at 75 °C.[11] However, the value is $[NaN_3]$ dependent (Table II); both ROH and ROEt are formed, and the very low percentage of RN_3 (0.4–0.6%) results in a large error in k_N/k_W. Our calculated k_N/k_W value (Table III) is at 100 °C in 75% aqueous dioxane, a solvent more similar to aqueous acetone, which gives only ROH and RN_3 and a higher (6–8%) $[RN_3]$ value.[11] A range of values is given since the values are $[NaN_3]$ dependent. The RHHS value of 1.7 for the 2-adamantyl system is in 80% EtOH where % RN_3 = 0.4 at 0.04 M NaN_3.[11] (Table II). The different k_N/k_W values for the 1- and 2-adamantyl systems reflect the k_E/k_W values of 0.40 for 2-adamantyl tosylate and 1.05 for 1-adamantyl bromide. We calculated k_N/k_W values of 32 (0.06 M NaN_3) and 16 (0.1 M NaN_3) in 75% dioxane at 75 °C where % RN_3 = 10–12%. However, the preferred value is 6.6 ± 0.5, measured for 2-adamantyl tosylate in 70% acetone/0.5 M NaN_3 at 77 °C[14] after the RHHS publication.

Two points in Ritchie's region were added to Table III, and the k_{solv} values for the chloro precursors had to be estimated. From log k_{solv} (40% EtOH–60% Et_2O, 25 °C) of $ArC(Cl)Ph_2$ and $ArCH(Cl)Ph$,[89] $\rho^+ = -2.60$ and -3.90, respectively. For $ArCH(Cl)Ph$, ρ^+ (85% acetone, 0 °C) = -5.72 from literature data.[61] Assuming a similar behavior of $ArC(Cl)Ph_2$ and extrapolation to 80% acetone, at 25 °C, gave $\rho^+ = -3.53$ (cf. Table III). On the assumption that the ratio of the ρ^+ values for substitution in the first and the second ring of Ar_2CHX is identical with those for substitution in the first vs. the second or third ring of Ar_3CCl, log $k_{solv}(An_3CCl) = 7.02$. For calculating $k_{solv}(p\text{-}O_2NC_6H_4N_2Cl)$ we assumed that, since the reactivities of An_3C^+ and $p\text{-}O_2NC_6H_4N_2^+$ toward nucleophiles do not differ very much,[19c,90] $k_{solv}(An_3CCl)/k_{solv}(p\text{-}O_2NC_6H_4N_2Cl) = k_W(p\text{-}O_2NC_6H_4N_2^+)$[90]$/k_W(An_3C^+)$.[19c]

Discussion

Revised log k_{solv} vs. log (k_N/k_W) Plot. Mechanistic Regions. The data of Table III are plotted in Figure 1. Various values for the same compound are connected by a line, and lines extending beyond a single point give the estimated range. Jencks' systems[25a] are represented by triangles and the RHHS slope is given for comparison. The plot is not linear, but when ignoring the troublesome systems, **10** and **17** (see below) and the points for systems reacting with N_3^- via S_N2,[25,33,68] it is approximately sigmoid with an appreciable spread of points. The slope of log k_{solv} vs. log (k_N/k_W) is very steep at the upper part, less steep in the middle, and steeper again or even inverted at the bottom. If the systems in region d are ignored (see below), the resulting "bell shaped" curve resembles very much the shape of Jencks' "predicted" RS plot for carbocations,[91a] and his points[25a] fit nicely with the rest of the data.

Phenomenologically, Figure 1 shows four (or five) distinguished regions that presumably reflect different mechanistic behaviors. (a) Ritchie's high k_{solv}-constant selectivity region. (b) A possible border region where the selectivity increases more than the reactivity of RCl but which may be due to an artifact. (c) A RS region where log (k_N/k_W) increases on increasing k_{solv}. (d) A low k_{solv} and nearly constant low selectivity region. (e) An inverted RS region where log (k_N/k_W) increases on decreasing k_{solv}. The borders of these regions are not well-defined, and we try below to delineate them and their mechanistic significance. We find it advantageous to follow Jencks[25,91] in analyzing the plot in terms of the rates of the individual capture processes and the lifetimes of the reaction intermediates. For the diffusion-controlled rate constants (k_{diff}) we used Jencks' estimation of 5×10^9 M^{-1} s^{-1},[25,92] and for the rate constant of molecular vibration we took $k = 10^{13}$ s^{-1}, implying that if a calculated rate constant exceeds this value, "the intermediate is not an intermediate".[91a]

Region a. The High k_{solv}-Constant Selectivity Region. Stable cations show a constant selectivity.[5] However, Johnson had suggested that deviations from Ritchie's plot are sufficient to account for the range of selectivity ratios observed in carbenium ion reactivities.[4c] Consequently, it is relevant to our work to question the constancy of the $N_+(N_3^-)$ values.

The first reported value (5.4) on the basis of $p\text{-}O_2NC_6H_4N_2^+$ was assumed to be a lower limit since the $ArN_2^+ + N_3^-$ reaction may not be rate determining.[90] Similar values (5.4 and 5.6) based on An_3C^+ were calculated by Ritchie in 1972[93,5a] from Bunton's data.[19c] We calculated values of 5.7 and 6.5, respectively, from Ritchie's recent data for $An_2C^+(o\text{-}C_6H_4SO_3^-)$ (PHRDME) and $An_2C^+(o\text{-}C_6H_4SO_2Me)$ (DAMS).[51] However, in a summary table in 1975 an $N_+(N_3^-)$ of 7.6 on the basis of the reaction of An_3C^+ was given.[5b] The new N_+ value arises[94] because water was dropped as a standard nucleophile since the water reaction was found to be general base catalyzed.[19a,e–g] Instead, for the three An_2C^+Ar ions, log k_{Nu} values were plotted against N_+ of HO^-, $MeONH_2$, and H_2NNH_2 and from the slope of the correlation line, and k_N $N_+(N_3^-)$ values of 6.4–7.6 were calculated.[94,95] An average of 12 values gives the best available N_+ value of 7.14 ± 0.37.[94] This procedure gave in our hands poor correlations with slopes of 0.92 for the three An_2C^+Ar ions. However, by using a larger number of nucleophiles with a wide range of N_+ values, we obtained better correlations with slopes of 0.76 ± 0.01. The N_+ values from the lines are 7.9 (An_3C^+), 7.6 (PHRDME), and 8.4 (DAMS), giving an average of 8.0 ± 0.3.

Hence, the $N_+(N_3^-)$ values, as well as the k_N/k_W values that are derived from them by multiplying by $[H_2O] = 55.5$ M, are nearly constant for the ions studied, although it is a question what is their best value. A RS behavior is not observed since $N_+(An_3C^+) \sim N_+(\text{PHRDME})$, although their reactivities toward nucleophiles differ greatly.[96]

Why are the $N_+(N_3^-)$ values constant? An explanation consistent with the RSP was offered by Pross.[18] We note that the basic requirement of Hammond's postulate[7] i.e., energy similarity of two consecutive species along the reaction coordinate, is mostly not fulfilled. $\Delta G^\ddagger$ values are high and differ appreciably from ΔG° values for both exothermic and endothermic reactions.[97] The

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(86) It is very difficult to analyze completely the literature data in an unequivocal way; e.g., some of the revised values of Table III differ somewhat from values published by us in the preliminary communications[2] either since we revealed new data or rechecked additional literature assumptions.

(87) Winstein, S.; Hojo, M.; Smith, S. *Tetrahedron Lett.* **1960**, 12. Winstein, S.; Gall, J. S.; Hojo, M.; Smith, S. *J. Am. Chem. Soc.* **1960**, *82*, 1010.

(88) RHHS's value (74), which was also used in the plot, is identical with the value reported in the same table for *p*-tert-butylbenzhydryl chloride.[11]

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(93) Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4966.

(94) Ritchie, C. D., private communication.

(95) We see no reason for dropping water as the standard nucleophile only for calculating $N_+(N_3^-)$ and not for other nucleophiles, e.g., CN^- or HO^-.

(96) In contrast with expectations on the basis of σ^+ values the reactivities of DAMS and PHRDME toward nucleophiles are 2 orders of magnitude lower than that of An_3C^+.[51] However, this may reflect steric effects on the k_{Nu} values.

(97) For the reaction of stable Ar_3C^+ with water, $\Delta G^\ddagger$'s (kcal·mol^{-1}, 25 °C) are between 23.5 for crystal violet and 16 for An_3C^+, whereas the ΔG°'s (kcal·mol^{-1}, 25 °C) change from 12.8 for crystal violet to 0.3 for DAMS.[19b,51] For reactions with N_3^- in water, $\Delta G^\ddagger$'s are between 11.8 (PHRDME) and 8.3 (An_3C^+) and ΔG° changes from -3.1 (PHRDME) to -6.5 (An_3C^+).[19c,51]

Table IV. k_N/k_{Cl} Values for Reactive Carbocations

no.[a]	compd	log k_{solv}[b]	k_N/k_W[c]	k_{Cl}/k_W (ref)	k_N/k_{Cl}
5	Ph_3CCl	1.34	10^5	3100[d] (41)	32
8	*p*-Tol_2CHCl	−1.66	227	384[e] (20)	0.59
			316	742[d] (20)	0.43
10	6-CMBP[f]	−2.03	4.10^4	1.33×10^4 [d] (22)	3.0
13	*p*-TolCH(Cl)Ph	−2.80	188	356[d,e] (20)	0.53
16	*p*-*t*-$BuC_6H_4CH(Cl)Ph$	−3.12	74	111[e] (20)	0.67
17	9-CMA[g]	−3.53	$4.5.10^4$	1950[d] (22)	22.8
19	Ph_2CHCl	−4.14	56	56[e] (20)	1.0[h]
25	*t*-BuCl	−5.70	12	7[i]–11[j]	1.7–1.1

[a] In Table III. [b] In 80% acetone at 25 °C, values from Table III. [c] From Table I or III. [d] From the decrease in k_{solv} in the presence of added Cl^-. [e] From the drift in k_{solv} during a run due to common ion rate depression. [f] 6-Chloromethylbenzo[a]pyrene. [g] 9-(Chloromethyl)anthracene. [h] Based on Ingold's data for both nucleophiles in 90% acetone. Other k_N/k_W values are given in Tables I and III. From the kinetic data of: Diaz, A. F.; Assamunt, N. *Tetrahedron* 1974, *30*, 797, in 90% acetone we calculated k_{Cl}/k_W of 22 ± 3. From Kohnstam's[21a] α_{Cl} value of 2.08 in 70% acetone we calculated $k_{Cl}/k_W = 35$. k_N/k_{Cl} values of 1.5–8 may also be calculated. [i] From exchange experiments in 60% aqueous acetone.[53] [j] Calculated from the data of: Schuster, R. H.; Schneider, I. A. *Rev. Roum. Chem.* 1973, *18*, 1841, in 50% dioxane, [KCl] = 0.66–1.33 M at 25 °C. The k_{Cl}/k_W ratios change strongly and unsystematically with [Cl^-], the solvent composition and the temperature and involve a relatively large error.

RS treatment may be unjustified[3a] if this is a case of a high intrinsic barrier where changes in the cation stability do not affect the position of the transition state in relation to the bond-making process. The constant selectivity may indicate that the process measured is mainly solvent reorganization[5d] and is therefore independent of R^+.

Regions b and c. The Border Region and the Apparent RS Region. Diffusion-Controlled N_3^-–R^+ Reaction. The reaction of N_3^- with Ritchie's stable cations is very rapid, but still $k_N \ll k_{diff}$. With the solvolytically generated less stable and presumably more reactive cations, k_N should increase. Consequently, a region where $k_N = k_{diff}$ is ~constant with all the cations should exist below the constant selectivity region. Any apparent RS behavior may then reflect a stability–reactivity relationship for the reactions of the various R^+'s with water alone, as suggested previously.[6a,24,25a,91] The problem is how to define the upper border of this region and whether it is directly below the constant selectivity region.

If the transition-state energy is sufficiently lowered before $k_N = k_{diff}$, a real RS behavior for pairs of nucleophiles could result for ions less stable than Ritchie's ions. We believe that either Ph_3C^+ or AnC^+HMe is close to the intersection point between the activation-controlled and the diffusion-controlled reaction with N_3^-, so that the shape of the plot between compounds 3 and **5** or 3 and 7 of Table III may reflect a RS behavior, i.e., decreased selectivity on increased reactivity of R^+. However, we note that Richard and Jencks[25a] assumed that reaction of R^+ dervied from compound **3** with N_3^- is already diffusion controlled. Moreover, since the data for compounds **3–6** require several extrapolations and may contain large errors, the shape of the plot in region b is not certain. The question of the existence of a border region should be probed with more accurate data. At present it seems that in the border region d log k_{solv}/d log $(k_N/k_W) < 1$, i.e., the selectivity increases faster than the "reactivity" in contrast with the opposite behavior in region c.

Different approaches give somewhat different answers concerning the position of Figure 1 at which k_N becomes diffusion controlled. First, in this region E_a for the N_3^- reaction should be close to zero, whereas E_a for the activation-controlled reaction with H_2O should be positive. Consequently, the selectivity can increase on increasing the temperature only when both processes are activation controlled.[98] Indeed, the selectivity of Ph_2CHBr decreases by 10% between 25 and 50 °C[41] (Table I), and the selectivities of *p*-$XC_6H_4CH(CMe_3)OMs$ (X = Me, *t*-Bu) are 6% lower at 35 °C compared with 7 °C. On the other hand, the selectivities of Tol_2CHCl (Table I)[38] and of camphene hydrochloride in MeOH[53] (where $k_{solv} \leq k_{solv}(Tol_2CHCl)$) increase with the temperature. Consequently, this approach suggests that region c is still not achieved for ions derived from compounds **3–7** of Table III, which are more stable than Tol_2CH^+. Moreover, it is likely that compounds significantly less reactive than *p*-Tol_2CHCl (i.e., compounds **9–14**) will still show an activated reaction with N_3^-.[99] This contrasts the conclusion reached below by other methods.[100]

Second, an approximate border for region c can be estimated by comparing the relative reactivities of N_3^- and a weaker nucleophile Nu^-. When N_3^- reacts by k_{diff} and Nu^- still reacts by an activation-controlled process, the k_N/k_{Nu} ratio will regularly decrease on increasing the reactivity of R^+. A k_N/k_{Nu} ratio of ca. 1 is obtained, regardless of R^+, when k_{Nu} becomes diffusion controlled. A comparison with Cl^- is pertinent, since the nucleophilicity of Cl^- ($n = 2.7$)[101] is lower than that of N_3^- ($n = 4.0$) in water in S_N2 reactions and possibly also in reactions with carbocations.[102] In Table IV we summarize the relevant data calculated mostly from common ion rate depressions.[103] Most of the data are due to Ingold et al.[20] so that in order to avoid confusion regarding the dependence on [H_2O], we compared their data for N_3^- and Cl^- at the same water concentration (compounds **16** and **19** in 90% acetone and compound **8** in both 85% and 90% acetone). The only k_N/k_{Cl} ratios that exceed unity are 32 for Ph_3CCl, 23 for 9-(chloromethyl)anthracene (9-CMA), and 3.0 for 6-(chloromethyl)benzo[*a*]pyrene (6-CMBP). All the other compounds for which $k_{solv} < k_{solv}(Ph_3CCl)$ show ratios close to unity, especially if errors in α values are considered. The higher k_N/k_{Cl} values for 9-CMA and 6-CMBP compared with those for compounds with similar or higher k_{solv} are not surprising since their k_N/k_W values deviate strongly from the line in Figure 1, and the $\alpha_{Nu} = k_{Nu}/k_W[H_2O]$ values for 6-CMBP in 50% acetone show an unusual order.[22] As seen from Table IV, according to this criterion the reaction of Ph_3C^+ may not be diffusion controlled,[104] but those of *p*-Tol_2CH^+ and more reactive ions derived from compounds below compound **8** in Table III are diffusion controlled.

Two additional compounds were not included in Table IV. For An_2CH^+ the log (k_N/k_W) for the mesitoate in MeOH[50] and the log (k_{Cl}/k_W) in 85% acetone[21a] give a k_N/k_{Cl} value of 3–4. A k_N/k_{Cl} value of ca. 1 can be calculated for camphene hydrochloride

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(98) For instance, if Ingold's "collapse" hypothesis[8a,20,38] holds and R^+ reacts with water from the solvation shell whereas N_3^- has to penetrate through this shell in order to react, $E_a(H_2O)$ may become lower than $E_a(N_3^-)$.

(99) The reaction of Cl^- with the cation formed in the solvolysis of Ph_2CCl_2, a compound with k_{solv} similar to those of compounds **12–14** in Table III, in 70% and 85% acetone, is probably not diffusion controlled since $E_a(Cl^-) - E_a(H_2O) = 1$ kcal·mol^{-1}.[21b]

(100) Golomb[39] who solvolyzed Tol_2CHCl under conditions very similar to Ingold's[38] found $[\% RN_3]_\infty = 50$ at 25 °C whereas Ingold's value is 60% at 0 °C.

(101) Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* **1953**, *75*, 141.

(102) The reported relative reactivities for capture of Ph_2CH^+ by nucleophiles in $MeNO_2$ are N_3^- (ca. 5) > Cl^- (2.96) (Pocker, Y. *J. Chem. Soc.* **1959**, 3939). However, these values may reflect diffusion-controlled values (cf. ref 99).

(103) Comparison of fewer compounds was reported previously by Swain[41] and by Huisgen (Huisgen, R. *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 751).

(104) The rate constants for the reactions of Cl^-, Br^-, and I^- with Ph_3C^+, Ph_2CH^+, and $PhCH_2^+$ in $ClCH_2CH_2Cl$ were determined by pulse radiolysis and found to be nearly the same (6×10^{10} M^{-1} s^{-1}); a diffusion-controlled reaction was suggested.[31]

Table V. Relative Reactivities of Nucleophiles toward R^+ and RX

substrate	Nu	solvent	k_{Nu}/k_N	ref
An_3C^+	$HOCH_2CH_2S^-$	H_2O	14	5c, 19c
	$HOCH_2CH_2SH$	H_2O	6.6×10^{-7}	5c, 19c
$An_2C^+(C_6H_4SO_2Me\text{-}o)$	$HOCH_2CH_2S^-$	H_2O	4.4	51
AnCH(OCOAr)Me	$MeOCOCH_2S^-$	50% TFE	0.6	25a
AnCH(OCOAr)Me	$MeCH_2CH_2SH$	50% TFE	0.33	25a
Ph_2CHCl	NCS^-	75% dioxane	1.6	39
Ph_3CCl	NCS^-	92% Me_2CO–2% dioxane–6% H_2O	0.14	41
An_3C^+	BH_4^-	H_2O	0.26	19c, 105
$c\text{-}C_3H_5CH_2OMs^a$	BH_4^-	66.67% diglyme	0.75 ± 0.25^c	56
$c\text{-}C_4H_7OMs^b$	BH_4^-	66.67% diglyme	0.78 ± 0.32^c	56
$1\text{-Me-}c\text{-}C_3H_4CH_2OMs^a$	BH_4^-	66.67% diglyme	2.3 ± 1.5^c	56
$1\text{-Me-}c\text{-}C_4H_6OMs^b$	BH_4^-	66.67% diglyme	2.4 ± 1.6^c	56

[a] $c\text{-}C_3H_5$, $c\text{-}C_3H_4$ = substituted cyclopropyl. [b] $c\text{-}C_4H_7$, $c\text{-}C_4H_6$ = substituted cyclobutyl. [c] Average values, since BH_4^- is lost in reaction with the liberated $MeSO_3H$.

in 80% aqueous $CH_2(OMe)_2$,[53] assuming that it gives an identical product distribution to that from norbornyl chloride. Both values are consistent with the above conclusion.

Scattered data for comparison with other nucleophiles in other media are given in Table V. Anionic thio nucleophiles gave $k_{RS^-}/k_N > 1$ with two of Ritchie's ions[5c,51] and a value <1 for reaction with AnCH(OCOAr)Me.[25a] Hence, the border between the activated and the diffusion-controlled regions is above compound **7** of Table III. $k_{BH_4^-}/k_W$ values are available for reactions with several cycloalkyl mesylates[56] and for An_3C^+,[105] but the similar reactivities of both nucleophiles with An_3C^+ give them little mechanistic value. In a RS study of the solvolysis of 1-phenylethyl derivatives Richard and Jencks[25a] used the low k_N/k_{RSH} value of 3 for AnCH(OCOAr)Me as evidence that the reaction of both nucleophiles with the derived cation or with more reactive ArC^+HMe cations of Table III are encounter controlled.

Finally, estimation of the k_W value for Ph_3C^+ and the k_N/k_W value enables calculation of a k_N value that can be compared with $k_{diff} = 5 \times 10^9$ M^{-1} s^{-1}. The log ($k_W[H_2O]$) (s^{-1}) values for three triarylmethyl cations are 1.11 ± 0.03 (An_3C^+), 1.98 ± 0.7 (An_2C^+Ph), 3.0 ± 0.3 (AnC^+Ph_2).[19b] If this additive trend continues, the extrapolated log ($k_W[H_2O]$) value is 4.0 ± 0.1 and $k_W(Ph_3C^+) = 150 \pm 30$ M^{-1} s^{-1}. This is a minimum value since the resonance stabilization of the anisyl-substituted cations may be mostly due to one anisyl group. For example, if the Hammett relationship for k_W takes the form $\log (k/k_0) = \rho(\sigma^+_{1st\ ring} + \sum\sigma_{2nd+3rd\ ring})$[106] the above data give $\rho = 3.51$, from which $k_W(Ph_3C^+) = 9.7 \times 10^3$ M^{-1} s^{-1}. Another estimation is based on the pK_R^+ values for trityl cations.[107] We calculated $\rho^+ = 5.28$ for substitution in the first ring, and $\rho^+ = 2.87$ for adding a *p*-MeO group to the second and third ring. If the same ρ^+ ratio is applied to the reaction of water with the same trityl cations we obtain $\rho^+ = 2.3$ for substitution in the first ring and then $k_W(Ph_3C^+) = 1100$ M^{-1} s^{-1}.

Different k_N/k_W values for Ph_3C^+ can be obtained by using different assumptions. If the constant selectivity region extends to Ph_3C^+, the expected k_N/k_W value will be 2.3×10^7 as found for An_3C^+.[19c] The much lower experimentally measured selectivity (Table III) may be due to experimental difficulties, such as insufficient mixing of the reaction mixture, or to the inequality $k_N \gg k_{diff}$, which necessarily reduces the observed k_N/k_W ratios. Alternatively, it may be assumed that the RSP operates and the k_N/k_W value for Ph_3C^+ is 3.1×10^5, which is the highest value observed.[41] Combination of the alternative k_N/k_W values gives six different k_N values ranging from 4.6×10^7 to 2.2×10^{11} M^{-1} s^{-1}. Using $k_W = 1100$ M^{-1} s^{-1} and $k_N/k_W = 3.1 \times 10^5$ gives $k_W = 3.4 \times 10^8$ M^{-1} s^{-1}, which we regard as a very probable value. In spite of the wide range of k_N values, a qualitative conclusion is still possible. Ph_3C^+ is either at the or close to the border between the activation-controlled and the diffusion-controlled regions. Since Ph_3C^+ was the most selective cation in the previous RS plots[10,11] the present results strongly support the suggestion[24] that the previous RS plots reflect only the increase in k_W when the stability of R^+ is decreased.[108]

The slope of log k_{solv} vs. log (k_N/k_W) at region c is therefore the slope of the log k_{solv} vs. −log k_W relationship. Arguments concerning the stability–reactivity relationship of carbocations suggest that it will be monotonous with a positive slope, but there is no compelling argument why it should be linear. The spread of the points in Figure 1, which may reflect the errors in the two parameters, makes it difficult to define the shape of a possible curve. However, the regression line fitting most of the data has a slope of 1.5,[109] a value that is much smaller than the previously reported ones.[10,11] The main reasons for the difference are the appreciably smaller k_N/k_W values used previously for Ph_3CCl and the use of points 39 and 54 for the 1- and 2-adamantyl systems by RHHS.[11]

Most of the difficulties associated with correlations of data from various sources should disappear on using only Richard and Jencks' data for the single class of compounds ArCH(X)Me[25a] with both electron withdrawing and donating substituents, although the selectivities were measured in 50% TFE–50% H_2O. When Tsuno's k_{solv} values[60] are plotted against the dimensionless k_N/k_W values, the five systems that react via S_N1 give an approximate linear relationship with a slope of 1.3 ($r = 0.987$). This slope is a ratio of two ρ^+ values: −5.7 for log k_{solv} vs. σ^+ and −4.3 for k_N/k_W vs. σ^3.[110,111] The slope is remarkably similar to that obtained above by using much more diverse systems.

Regions d and e. Lifetime of the Cationoid Intermediate. A Shift from S_N1 to S_N2 Mechanism. When $k_N = k_{diff}$ an increase in the reactivity of R^+ still increases k_W and at the limit it should also be diffusion controlled. This should result in a k_N/k_W ratio of unity so that the lower part of the plot should coincide with the log k_{solv} axis. This was not observed experimentally, as already noted by RHHS.[11] One possibility is that as k_{solv} decreases, the stability and the lifetime of the intermediate also decrease and when k_N reaches and exceeds 10^{13} s^{-1} (the rate of molecular vibration)[91] the intermediate does not exist anymore,[91a] and an alternative concerted route, first order in N_3^- with a selectivity

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[105] Bunton, C. A.; Huang, S. K.; Paik, C. H. *J. Am. Chem. Soc.* **1975**, *97*, 6262.

[106] The only similar analysis known to us is due to: Hegarty, A. F.; Lomas, J. S.; Wright, W. V.; Bergmann, E. D.; Dubois, J. E. *J. Org. Chem.* **1972**, *37*, 2222, who used with limited success a similar equation for treating substituent effects in the bromination of 1,1-diarylethylenes substituted in the two rings. For a related treatment in elimination reactions see: McLennan, D. J.; Wong, R. J. *J. Chem. Soc., Perkin Trans. 2* **1972**, 279.

[107] Cook, M. J.; Dassanayake, N. L.; Johnson, C. D.; Katritzky, A. R.; Toone, T. W. *J. Am. Chem. Soc.* **1975**, *97*, 760.

[108] In a previous work k_W and k_N values on the basis of the assumption of additivity for k_W and on the selectivity of An_3C^+ were reported.[24b] However, they included an error in the $[H_2O]$ term.

[109] For 14 systems (compounds **5**–**23**, excluding Jencks' systems[25a] and compounds **10**, and **17**) the slope is 1.48 ($r = 0.967$); if Jencks' compounds are included, the slope = 1.45 ($r = 0.857$). In both cases, log $k_{solv} = -6.2$ at log (k_N/k_W) = 0.

[110] The ρ^+ values for the solvolysis of $ArC(Cl)Ph_2$ in 80% acetone at 25 °C (−3.53) and for the reaction of ArC^+Ph_2 with water (+2.3) give a similar ratio of 1.5.

[111] In contrast, a log k_{solv} vs. log (k_N/k_W) plot for the benzhydryl systems is scattered, probably reflecting the approximations in deriving the data.

>1, is enforced on the reaction. Another possibility is a preassociation stepwise route. According to Jencks[91b] "when the intermediate does not exist or is too unstable to diffuse through the solvent, the reaction must occur through a preassociation mechanism in which the reactants, including the final reactant or catalyst, are assembled before the bond-making or -breaking step occurs". If N_3^- or the ion pair $M^+N_3^-$ stabilize the transition state for the ionization, the opportunity to form RN_3 may increase (see below) resulting in a $k_N/k_W > 1$. The mechanistic questions are therefore at what stage in Figure 1 k_W becomes diffusion controlled and $k_N[N_3^-]$ becomes larger than 10^{13} s^{-1} and which of these two situations appears earlier?

A likely estimate can be derived by extrapolating the approximate linear relationship in the diffusion-controlled region of Figure 1 to log $(k_N/k_W) = 0$ where $k_N = k_W = k_{diff} = 5 \times 10^9$ M^{-1} s^{-1}. This extrapolation gives $k_{solv} \sim 10^{-6}$ s^{-1} as the value below which the $R^+ + H_2O$ reaction is diffusion controlled. A similar value is obtained by using Jencks' compounds **3**, **7**, **11**, **14**, and **21** in Figure 1. Inspection of the line suggests that the error in k_{solv} does not exceed 1 order of magnitude. Consequently, in the absence of special factors that were not included in this treatment, all the compounds below compound **26** in Table III that react via S_N1 would react with $k_W = k_{diff}$.

Since $[H_2O] = 11.2$ in 80% acetone, R^+ will cease to be an intermediate in water when $k_W \geq 10^{12}$ M^{-1} s^{-1}. Further extrapolation of the linear relationship indicates that this will occur when $k_{solv} \leq 10^{-10}$ s^{-1}, i.e., for compounds **45–54**, including 2-adamantyl chloride.

The measured rate with N_3^- is dictated by the condition $k_N = k_{diff}$, but for calculating when $k_N[N_3^-] \geq 10^{13}$ s^{-1}, the inherent nucleophilicity of N_3^- (rate constant k_N^{in}), which is free from the above limitation, is required. The ordinary N_3^- concentration studied is ca. 0.1 M, i.e., the k_N^{in} value at which the switch over to a concerted process is expected, is 10^{14} s^{-1}. For estimating the unknown k_N^{in} values the "inherent" selectivities of R^+ toward N_3^- and H_2O are required.

One possible assumption is that Ritchie's constant selectivity is inherent for all the R^+s, but it is not observed experimentally when $k_N = k_{diff}$. In this case $k_N/k_W = 2.3 \times 10^7$ as found for An_3C^+, and $k_N \geq 10^{14}$ s^{-1} when $k_W \geq 4 \times 10^6$ s^{-1}. From Figure 1 and the above calculations this value is already reached for the systems immediately below Ph_3CCl, in contrast with Ingold's kinetic data[20] and McLennan's observation[42] that k_{solv} is independent of the $[N_3^-]$ in the reaction of Ph_2CHCl with N_3^-. Although this possibility is supported by Shafer and Harris'[112] conclusion that a solvent participation may be important in the solvolysis of Ar_2CHCl in aqueous EtOH, we agree with McLennan's recent conclusion[113] that nucleophilic solvent participation in this system is absent. Otherwise, the reaction with the much better nucleophile $[N_3^-]$ should be of an overall second order, in contrast with the experimental observation.[114]

A less extreme assumption is that k_N^{in}/k_W is nearly constant for unstable cations, being 3.1×10^5, the highest value measured for Ph_3C^+. This may be supported by the near constancy of the Winstein–Grunwald *m* values and the Hammett ρ values in the solvolysis of $Ar_2CHOPNB$.[113] In this case a concerted reaction with N_3^- is expected for systems with $k_{solv} \leq 10^{-5}$ s^{-1}, i.e., for 2-methyl-2-adamantyl chloride and systems below it. Consequently, the $R^+ + H_2O$ reaction becomes diffusion controlled at approximately the same structural region where the reaction with N_3^- becomes concerted, and hence a log (k_N/k_W) value of 0 is not obtained. Indeed, the lowest value (0.52) is for the 2-methyl-2-adamantyl system.[14] In this case we may attribute the higher values for several of the lower systems in Figure 1 (region e) to a direct attack of N_3^- on RX. We note that the deviation from linearity of log k_{solv}(*t*-BuX) vs. log k_{solv}(1-adamantyl-X), X = Cl, Br, in media of low nucleophilicity led Bentley et al.[79,115] to the conclusion that solvolysis of *t*-BuX in nucleophilic solvents involves nucleophilic solvent assistance. Hence, an S_N2 reaction with N_3^- should not be surprising.[116]

The intervention of an S_N2 process is supported by Jencks' data.[25] The evidence for an S_N2 reaction (second-order kinetics and positive ρ for the selectivity) starts with compound **24** of Table III, which is very close in reactivity to the 2-methyl-2-adamantyl system (compound **23**). Other compounds that are known to react with N_3^- via S_N2 and show increasing log (k_N/k_W) with the decrease in k_{solv} are the benzyl chlorides (**20** and **27**),[68,70] the secondary chlorides (**40** and **41**),[33] and 2-aryl-1-propyl tosylates in their reaction to form the primary products (**51**, **52**, and **53**).[33] The points for all these compounds are near the S_N2 line, which we drew for Jenck's systems. Nair's 1-arylneopentyl mesylates ArCH(X)R (systems **30**, **31**, **35**, and **43**, X = OMs, R = *t*-Bu)[77] structurally resemble Jencks' compounds where R = Me, but their selectivities are lower. Although the kinetic order in N_3^- was not reported, the small selectivity increase on decreasing k_{solv} or on decreasing the solvent polarity fit an S_N2 process.[77] The deviation from Jencks' S_N2 line may result from an earlier transition state for the reaction with N_3^-, due to steric hindrance by the bulky *tert*-butyl group to nucleophilic approach.

The conclusion that systems with $k_{solv} \leq 10^{-5}$ s^{-1} react by a concerted process with N_3^- raises two questions. First, why a second order reaction with N_3^- (i.e., $k_{obsd} = k_{solv} + k_N[N_3^-]$) was not observed for all the compounds below compound **23** in Table III? Second, why do the cycloalkyl derivatives **29**, **32**, **33**, **36**, **39**, **42**, **50**, and **54** form a new rgeion (region d) of low and approximate selectivity to that of compounds **25** and **26**, i.e., log $(k_N/k_W) = 1.2 \pm 0.2$?

The answer to the first question (which arises also when assuming a preassociation stepwise mechanism) is that when the selectivities are low the contribution of the $k_N[N_3^-]$ term to k_{obsd} is small at low $[N_3^-]$ and can escape detection. In fact, addition of N_3^- to solvolyzing systems did increase the reaction rate, but it is difficult to distinguish a possible second-order term from a salt effect on k_{solv} whose magnitude and even its direction are unknown or in dispute.[48b] This is demonstrated in four compounds: (a) With *t*-BuBr in 90% Me_2CO addition of 0.1 M N_3^- raised the initial rate by 1.4-fold, a similar effect to that of NaBr or NaCl.[75] However, as the percent RN_3 in the total product is only 6–10%, a large effect on k_{obsd} is not expected. (b) With cyclopropylmethyl mesylates in aqueous diglyme NaN_3 gives higher acceleration than LiCl[14] but the difference is too small if all the RN_3 is formed via a second-order process. (c) For 1-adamantyl bromide, and 2-adamantyl tosylate, the observed percent RN_3 values in 80% EtOH are at least 1 order of magnitude smaller than the calculated values from rate increase assuming a second-order process.[11] The *b* values are not high (1.2–2.1 and 2.7–4.1, respectively) but the percent RN_3 are so low that kinetic arguments cannot be used to exclude second-order formation of RN_3. In 75% dioxane[11] the percent RN_3 is still 2-fold lower than the expected value on the basis of rate acceleration so that a combination of a salt effect of NaN_3 on the S_N1 route and its second-order reaction with RX is possible. Indeed, slow second order reaction of N_3^- with 2-adamantyl-OBs in toluene was recently reported.[117]

The low and similar selectivities of most of the cycloalkyl systems do not necessarily arise from the same reason, as these compounds are tertiary (**29** and **39**), secondary (**33**, **36**, **42**, **50**, and **54**), and primary (**26** and **32**) with different degrees of

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(112) (a) Shafer, S. G.; Harris, J. M. *J. Org. Chem.* **1981**, *46*, 2164. (b) Cf. also: McLennan, D. J.; Martin, P. L. *Tetrahedron Lett.* **1973**, 4215; *Aust. J. Chem.* **1979**, *32*, 2361.

(113) (a) McLennan, D. J.; Martin, P. L. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1091; (b) *Ibid.* **1982**, 1099.

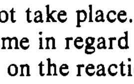
(114) Shafer and Harris[112] were also concerned about the contradiction with the kinetic evidence in the reaction with N_3^-.

(115) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Am. Chem. Soc.* **1979**, *101*, 2486.

(116) For an opposing view that in the solvolysis of *tert*-butyl halides nucleophilic assistance is relatively unimportant see: Abraham, M. H.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1981**, *46*, 3053. For an undecided position concerning nucleophilic assistance in the solvolysis of *tert*-butyldimethylsulfonium ion see: Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, *23*, 4635.

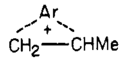
(117) Banert, K.; Kirmse, W. *J. Am. Chem. Soc.* **1982**, *104*, 3766.

neighboring group participation in the solvolytic transition state and of hindrance to approach of the nucleophile to RCl or R^+. One possible explanation is that due to hindrance of concerted attack from the rear and its unfeasibility from the front,[118] the concerted reaction does not take place. Instead, the formation of an ion pair whose lifetime in regard to N_3^- attack is $\gg 10^{-13}$ s^{-1} is "sterically enforced" on the reaction. Since attack on sterically hindered ion pairs from the rear is still difficult, N_3^- must attack them from the front. In the absence of an electronic barrier to the reaction, the rate of this attack is limited by the diffusion-controlled departure rate of the nucleofuge from the front. A stepwise substitution via the very reactive carbocations where $k_W > k_{diff}$ must involve a preassociation with N_3^- or $M^+N_3^-$. This may stabilize the transition state for ionization for which **1** is a possible description[119] and lead to a small preference for formation of RN_3 (i.e., log $(k_N/k_W) > 0$). The recently observed second-order reaction of 1-adamantyl tosylate with PhONa in THF[120] was interpreted as reflecting a front-side assistance to the ionization process, presumably by a transition state similar to **1**.



1

A related explanation is based on the suggestion that the product-forming intermediate for most of the cycloalkyl compounds in region d is bridged. It is believed that *exo-* and *endo*-2-norbornyl derivatives solvolyze in aqueous organic media mainly via the same carbocation,[78,84,121] which may be bridged.[122] It was recently suggested that cyclooctyl tosylate solvolyzes via an hydrogen-bridged cation,[82,83a,123] and similar nonclassical ion pairs are probably formed from the isomers **26** and **29** or from the isomers **32** and **36**.[56,124,125] A bridged intermediate was also proposed for 1-methyl-2-adamantyl tosylate.[83b] log (k_N/k_N) values greater than unity in region d, where the intermediate cations (if formed at all) should be very unstable, may also result from the formation of bridged ion pairs that are attacked from the front by the waiting N_3^-. In these species nucleophilic approach from the front may be less hindered than from the back, especially since the nucleofuge shields simultaneously the approach to several reaction sites. Our explanation is supported by the behavior of the phenonium ions **2** that are formed in a k_Δ process from 1-aryl-2-propyl and 2-aryl-1-propyl tosylates.[33,126] In Figure 1, the log (k_N/k_W) values for ions **2** derived from compounds **37**, **38**, **44**, **45**, **48**, and **49** are between the approximate constant low-selectivity line passing through *tert*-butyl, 1- and 2-adamantyl systems and the S_N2 line for the relatively unhindered secondary substrates, whereas the other ions of region d are nearer to the former. It seems that the reaction of the bridged ions of region d have features that resemble a classical S_N2 process. This is expected since for them the cation–nucleophile combination is concerted with the cleavage of the carbon–carbon bond of the bridge. This concerted reaction is more favored with the N_3^-, thus resulting in a selectivity higher than unity.



2

Isomeric precursors in region d such as *exo-* and *endo*-2-norbornyl, cyclopropylmethyl, and cyclobutyl derivatives and 1-aryl-2-propyl and 2-aryl-1-propyl derivatives, which presumably give similar product-forming bridged cations, should show similar k_N/k_W values. This was assumed to be the case for the arylpropyl derivatives[33] and was experimentally observed for the several cyclopropylmethyl–cyclobutyl pairs.[56] *endo*-Norbornyl gave higher selectivity than the *exo*-isomer.

What is the k_{solv} value that should be used as a stability measure of the common intermediate? The isomers give differing k_{solv} values that reflect ground- and transition-state energy differences. For the norbornyl isomers it was suggested that log k_{solv}(exo) is a better measure of the bridged ion stability.[29] We included in Figure 1 the k_{solv} values for both isomers in all the above mentioned systems, and this resulted in an increased scatter of the points.

The low-selectivity values of the less hindered compounds in region d may also result from a concerted reaction that involves a loose transition state with a low extent of C–nucleophile bond formation (i.e., an "uncoupled concerted mechanism"[91b]). The low k_N/k_{SOH} value of 5 for the inverting solvolysis of 3β-cholestanyl-OBs in 66.7% EtOH[14] fits this explanation. The second-order rate constants for substitution of ArCH(Cl)Me with electron-withdrawing substituents by N_3^- give a high negative ρ^+ value of -3.3,[25b] a value that is consistent with a very loose transition state.

Rear-side attack by N_3^- on *endo*-2-norbornyl tosylate is sterically allowed,[117] and the solvolysis was suggested to be slightly nucleophilic assisted.[78] A rearside attack by N_3^- on *exo*-2-norbornyl tosylate is also possible, as an inverted product is obtained in a second-order reaction with N_3^- in toluene, with a rate constant only 2 times smaller than for the endo isomer. The absence of deuterium scrambling during the solvolysis of the exo isomer[117] and other results point to a concerted reaction, which can also be feasible in aqueous acetone. However, increase in the solvent polarity may change the mechanism. Indeed, the second-order reaction of *exo*-2-norbornyl tosylate with PhONa in the more polar THF is accompanied by a complete deuterium scrambling.[120] It was suggested that the reaction proceeds via electrophilically salt-assisted ionization to form an ion pair.[120] This may be termed "preassociation stepwise mechanism".[91b]

Several reservations concerning the discussion above can be raised. First, points in region d may be misplaced since their log k_{solv} reflects not only the stability of the cationoid intermediate (i.e., $k_{solv} = k_c$ or k_Δ) but also a varying contribution of a solvent-assisted process k_s.[127] Such a contribution was suggested for *t*-BuBr[79,115,116] and *endo*-2-norbornyl tosylate,[78] and it may be responsible for the higher k_{solv} values of the primary systems **26** and **32** compared with the secondary systems **29** and **36**. Hence, for these systems the k_{solv} values in Figure 1 are above

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(118) Anh, N. T.; Minot, C. *J. Am. Chem. Soc.* **1980**, *102*, 103. Gray, R. W.; Chapleo, C. B.; Vergnani, T.; Dreiding, A.; Liesner, M.; Seebach, D. *Helv. Chim. Acta* **1975**, *58*, 2524 and references therein. For the special case of cyclopropane, see: Turnkenburg, L. A. M.; de Wolf, W. H.; Bickelhaupt, F.; Stam, C. H.; Konijn, M. *J. Am. Chem. Soc.* **1982**, *104*, 3471 and references therein.

(119) Perrin, C. L.; Pressing, J. *J. Am. Chem. Soc.* **1971**, *93*, 5705.

(120) Takeuchi, K.; Kato, Y.; Moriyama, T.; Okamoto, K. *Chem. Lett.* **1981**, 935.

(121) (a) Raber, D. J.; Neal, W. C.; Dukes, M. D.; Harris, J. M.; Mount, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 8137. (b) Bentley, T. W.; Bowen, C. T.; Marten, D. H.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5466.

(122) We discuss here the consequences of the suggested bridging in the *exo*-2-norbornyl system without offering any new data related to the controversy concerning bridging in these systems. For recent reviews concerning and challenging the concept of bridging in the norbornyl derivatives see: Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977. Brown, H. C. "International Symposium on Organic Reaction Mechanisms. New Concepts and Prospects", Kyushu University, Fukuoka, Japan, August 18–21, 1982, Abstr pp 5–20.

(123) Harris, J. M.; Mount, D. L.; Smith, M. R.; McManus, S. P. *J. Am. Chem. Soc.* **1977**, *99*, 1283.

(124) Majerski, Z.; Nikoletic, M.; Borcic, S.; Sunko, D. E. *Tetrahedron* **1967**, *23*, 661.

(125) Concerning the question whether these systems are classical or nonclassical see: Olah, G. A.; Jeuell, C. L.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 146. Olah, G. A.; Liang, G.; Babiak, K. A.; Ford, T. M.; Goff, D. L.; Morgan, T. K., Jr.; Murray, R. K., Jr., *Ibid.* **1978**, *100*, 1494. Olah, G. A.; Surya Parkash, G. K.; Donovan, D. J.; Yavari, I. *Ibid.* **1978**, *100*, 7085 and references therein.

(126) We note that the order of the k_N/k_W values for the k_s process for $ArCHMeCH_2OTs$ Ar = An > Ph > Tol do not follow the order of Hammett's substituent contants, whereas the values for $ArCH_2CH(OTs)Me$ follow the expected order Ph > Tol > An. For the k_Δ process the order is An > Ph > Tol for both isomers. We wonder if the differences are due to small errors involved in the separation of k_{solv} to its k_Δ and k_s components.

(127) Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89.

the expected position on the basis of the cation stability, and the corrected values may cover a much narrower range.

Second, extrapolation of the approximate linear line of region c to very low k_{solv} values may be unjustified, so that we cannot decide when $k_W > k_{\text{diff}}$. However, the low selectivity of the relatively stable 2-methyl-2-adamantyl cation, where $k_N \gg k_{\text{diff}}$, suggests that k_W cannot differ much from k_{diff}. It should exceed it for the less stable cations in regions d and e. Finally, if the inherent selectivity log (k_N^{in}/k_W) obeys the RSP it should decrease on decreasing k_{solv}, and its value at low k_{solv} should be much lower than 3×10^5. In this case $k_N[N_3^-]$ will not reach 10^{13} s^{-1} much before this value is reached by $k_W[H_2O]$, so that the concerted route will not be enforced on all the systems in these regions, and it may take place only for the less hindered primary and simple secondary derivatives.

In conclusion, we believe that the selectivities in region d reflect mainly a stepwise reaction via an ion pair whose formation is assisted by a preassociation with $M^+N_3^-$ or with N_3^-. In some cases a concerted reaction with a low extent of C–Nu bond formation in the transition state may replace or operate in parallel to the stepwise route. The actual selectivity values may decrease on increasing the steric hindrance of approach to the positive reaction site. For example, the methyl-bridged cation derived from compounds **26** and **29** is more hindered than the unsubstituted cation derived from compounds **32** and **36**, and the selectivity of the former is indeed lower. Other important factors affecting the selectivity are the stability of the cationoid part, the nature of the ion pair and its solvation, the degree of electrophilic assistance to the ionization, the possibility of a general base catalysis by N_3^- and the nucleofuge to the water reaction, and the structure of a possible concerted transition state. Our knowledge of the importance of these effects in general and their dependence on the structure of R^+ is small. Further analysis seems too speculative and should wait until further experimental data are available.

Conclusions

The extended log k_{solv} vs. log (k_N/k_W) plot is not linear. Phenomenologically, it comprises of regions of nearly constant selectivity, both high and low, of apparent reactivity–selectivity, and of inverted RS behavior. Analysis of the plot in terms of the intermediates lifetimes suggests that the reactions of most of the intermediate carbocations with N_3^- are diffusion controlled. The approximate linear RS behavior over an appreciable structural range is due to the reactivity–stability relationship between log k_{solv} and k_W. For systems that give very reactive R^+ the reaction is either concerted or proceeds via a preassociation stepwise route. Steric effects seem to be important in determining the existence of cationoid intermediates and their lifetimes. Ion pairs play an important role in the overall solvolysis reaction, and since they are involved in many of the reactions that define the approximate RS line, conclusions concerning the intermediacy of ion pairs that are based on the linearity of the line or deviations from it[9g,10] should be drawn with extreme caution.[2b] The extrapolations for temperature, solvent, nucleofuge, and other parameters that are required for obtaining the plot may be responsible for the appreciable scatter of the points. New data that should be measured under more similar conditions for all compounds will possibly reveal mechanistic aspects that are lost due to the present extrapolations.

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Registry No. 1, 14368-49-1; **2**, 49757-42-8; 3, 86696-30-2; **4**, 7525-23-7; **5**, 76-83-5; **6**, 82022-42-2; **7**, 1538-89-2; **8**, 13389-70-3; **9**, 86696-31-3; **10**, 49852-84-8; **11**, 58114-01-5; **12**, 51830-43-4; **13**, 779-14-6; **14**, 19935-80-9; **15**, 63537-05-3; **16**, 19767-95-4; **17**, 24463-19-2; **18**, 6196-85-6; **19**, 90-99-3; **20**, 824-94-2; **21**, 2362-36-9; **22**, 134-83-8; **23**, 37723-65-2; **24**, 456-16-6; **25**, 507-20-0; **26**, 10523-77-0; **27**, 4039-92-3; **28**, 58114-05-9; **29**, 10523-97-4; **30**, 73492-32-7; **31**, 86696-32-4; **32**, 5911-08-0; **33**, 765-91-3; **34**, 19935-76-3; **35**, 1688-17-1; **36**, 1120-57-6; **37**, 4125-46-6; **38**, 34197-99-4; **39**, 935-56-8; **40**, 75-29-6; **41**, 628-61-5; **42**, 1556-08-7; **43**, 86696-33-5; **44**, 20983-44-2; **45**, 826-00-6; **46**, 20488-11-3; **47**, 19935-75-2; **48**, 10304-81-1; **49**, 824-47-5; **50**, 2999-06-6; **51**, 34197-99-4; **52**, 826-00-6; **54**, 7346-41-0; Ph_2CHBr, 776-74-9; Ph_3CBr, 596-43-0; Ph_3CF, 427-36-1; Ph_3COAc, 971-85-7; Ph_3CSCN, 35036-90-9; *p*-TolCH(Ph)OPNB, 32435-32-8; *p*-AnCH(Me)OPNB, 58287-11-9; c-C_5H_9OMs, 16156-57-3; *p*-$Me_2NC_6H_4CH(Me)SC_6H_3Cl_2$-3,5, 86696-34-6; *p*-$Me_2NC_6H_4CH(Me)OAc$, 26921-60-8; $An_2CHOCOC_6H_2Me_3$-2,4,6, 36366-56-0; *p*-$ClC_6H_4CH(OPNB)Ph$, 54059-78-8; *t*-BuBr, 507-19-7; c-C_5H_9-OTs, 3558-06-3; c-C_6H_{11}-Cl, 542-18-7; c-C_8H_{15}-OBs, 28074-08-0; c-C_8H_{11}-OTs, 6597-09-7; $HOEH_2CH_2S^-$, 57966-62-8; $HOCH_2CH_2SH$, 60-24-2; $MeOCOCH_2S^-$, 64743-45-9; $MeCH_2CH_2SH$, 107-03-9; NCS^-, 302-04-5; BH_4^-, 16971-29-2; An_3C^+, 14039-13-5; $An_2C^+(C_6H_4SO_2Me$-*o*), 86709-63-9; c-$C_3H_5CH_2OMs$, 696-77-5; c-C_4H_7Oms, 22524-45-4; 1-Me-c-$C_3H_4CH_2OMs$, 697-52-9; 1-Me-c-C_4H_6OMs, 935-20-6; Bu_4NN_3, 993-22-6; EtOH, 64-17-5; NaN_3, 26628-22-8; N_3^-, 14343-69-2; H_2O, 7732-18-5; 1-adamantyl bromide, 768-90-1; 2-adamantyl tosylate, 25139-43-9.