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SOME QUESTIONS ON THE INTERPRETATION OF THE EFFECTS OF SODIUM AZIDE ON NUCLEOPHILIC SUBSTITUTION IN THE MECHANISTIC BORDERLINE REGION

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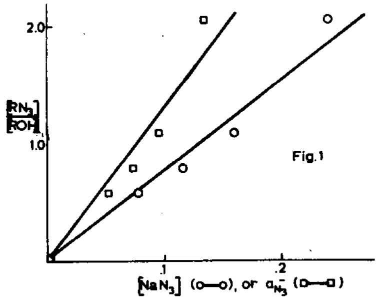
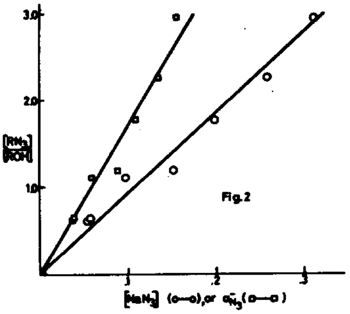
A mechanistic model for borderline solvolyses, which includes a unification of S_N1 and S_N2 as well as E1 and E2 mechanisms, has been advanced in recent years by Sneen and coworkers.[1] The main evidence for initial support of this model, or theory, came from their study of the effects of added sodium azide on the kinetics and products of solvolysis of 2-octyl sulfonate esters in aqueous dioxane solutions.[2]

Even though this model introduced a change of views on solvolyses in the direction of our own "unified mechanism,"[3] some of its features disagreed with those of ours. This made us question their proposed unification of solvolysis mechanisms and the arguments used to support it. This communication deals with the question of their interpretation of salt effects on the reaction products and rate.

The essence of the experimental support for the proposed theory was provided by the observation that the total rate of reaction, k_{exptl}/k_{NA}, of 2-octyl mesylate in the presence of sodium azide in 25 and 30% aqueous dioxane was intermediate between zero and first order in azide ions, and that this rate fit equation ie that described the proposed scheme.[2] However, the above conclusion was arrived at by using the molar amount of added sodium azide as a measure of azide ions; that is, by apparently making the assumption, although this was not explicitly stated, that the dissociation of this "strong" electrolyte is complete, and that activities are equal or proportional to concentrations. Evaluation of this tacit assumption led us to the conclusion that it may be far from justified.[4a] For the purpose of this communication suffice to point out that the concentration range of salt, up to 0.311 M, used in their studies extends into the region of significant deviations from the applicability of the Debye-Hückel law.[5a] These deviations may be partly described as, or be considered equivalent to, incomplete dissociation.[5a] Furthermore, activity coefficients of salts drop sharply in that range, even in water;[5b,4a] that of azide ion drops to 0.81 at 0.03 M, and to 0.68 at 0.2 M aqueous solution.[5d] The drop is even greater in aqueous dioxane.[4a,b]

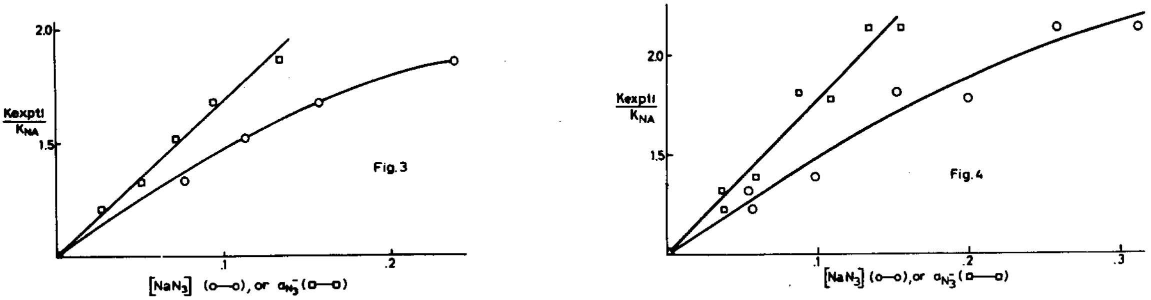
We suggest that the use of concentrations of salts instead of activities is unjustified. In a footnote of a recent publication on the solvolysis of the α-arylethyl halide system in the presence of sodium azide,[6] Sneen commented: "... the linearity of product plots (RN_3/ROH vs. sodium azide concentration) serves one other important and useful function; it establishes that, at the concentration levels of salt employed in these studies (0.113 M), concentrations must be proportional to activities." Similar linear plots also appeared in the 1969 publication under discussion.[2] Presumably, these linear plots also provided the justification for the use of concentrations instead of activities. It is instructive, however, to compare the product plots vs. sodium azide concentrations with those vs. the corresponding azide ion[7] activities.[4a,b] (Figs. 1 and 2). Interestingly enough, either type of plot for the 30% aqueous dioxane solvolysis can be fitted by a straight line! The data for the 25% aqueous dioxane reactions give less satisfactory straight line plots.[8] Such plots do not provide a sensitive enough test of the question of proportionality[9] between concentrations and activities, at least for the range and scatter in the reported product data. Nor do they justify the use of concentrations instead of activities, especially in the face of evidence against such proportionality.[4,5]





Figures 1 and 2. Plots of $[RN_3]$ / $[ROH]$ | vs. $[NaN_3]$ (from ref. 2), and vs. the corresponding azide ion activities, α (4a,b), for the reaction of 2-octyl mesylate with sodium azide and water in 25 (Fig. 1) and 30 (Fig. 2) vol % aqueous dioxane. The least square fits (solid lines) of the experimental points have slopes and correlation coefficients which are respectively: Fig. 1: (plot vs. $[NaN_3]$) 7.72 and 0.989; (plot vs. α) 12.97 and 0.976. Fig. 2: (plot vs. $[NaN_3]$) 9.35 and 0.991; (plot vs. α) 17.23 and 0.983.

Having established this much, we now plot the reported rate data against azide ion activities, as an approximation to a more realistic approach to the problem, and compare these plots with those against concentrations (Figs. 3 and 4). The plots are quite revealing. The curved plots become straight lines![7,10] This is most significant as it suggests, at least for the data reported,[2] that the rate of destruction of the starting material, is first order in azide ion, and not between zero and first order as concluded. Furthermore, these rate data can not fit the rate equation describing the proposed scheme (eq. 1e),[2] even with any adjustment of the variable x of this equation, other



Figures 3 and 4. Plots of k_{exptl}/k_{NA} (12) *vs.* [NaN_3] (from ref. 2), and *vs.* azide ion activities (4a,b), in 25 (Fig. 3) and 30 (Fig. 4) vol % aqueous dioxane. The curved lines are the best fits of the plots *vs.* [NaN_3] and correspond to the theoretical plots given in ref. 2. The straight lines are the least square fits of the plots *vs.* activities; their slopes and correlation coefficients are respectively: (Fig. 3): 6.90 and 0.994; (Fig. 4): 7.73 and 0.982.

than one rendering the process into a second order one ($\underline{x} \to \infty$).[6] This is so because this equation describes mathematically a curve for any process other than a first ($\underline{x} \to 0$) or second ($\underline{x} \to \infty$) order one.[6]

The above considerations suggest that the solvolysis of 2-octyl mesylate in 25 and 30% aqueous dioxane — the very system studied most and chosen to prove the theory — does not necessarily provide evidence for the proposed scheme.[1,2] One may argue that this system happens not to give borderline behavior — in which case the proposed scheme is not distinguishable from traditional S_N2 or S_N1 mechanisms by this kinetic approach;[2] and that the other substrates studied later in the same laboratory[1] are sufficient to support the theory.[11] It should be pointed out, however, that the slopes of the rate plots differ from, and are smaller than, those of the corresponding product plots — being 6.90 *vs.* 12.97, and 7.73 *vs.* 17.23 for the 25 and 30% aqueous dioxane media respectively. This difference suggests that this reaction is not a simple S_N2 one. That it is not a simple S_N1 either, is supported by the fact that azide appears in the products, and has also a much higher effect on the rate than the salt effects observed[2] for this system. Thus the solvolysis of the 2-octyl system should be classified as a borderline one; but then, here is an example of a *borderline* solvolysis failing to obey the curved rate plots, even though such a solvolysis is predicted and *required* by Sneen's theory to obey them.

An explanation of these observations in terms of our "unified mechanism"[3] will appear elsewhere.[8b]

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REFERENCES and FOOTNOTES

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2. R.A. Sneen and J.W. Larsen, J. Amer. Chem. Soc., 91, 362 (1969); Ibid., 88, 2593 (1966).
3. (a) G.A. Gregoriou, Chimika Chronika, A 23, 172 (1958); C.A., 53, 193a (1959); (b) G.A. Gregoriou, 1962 to 1968 references cited in ref. 3c; (c) S.L. Loukas, M.R. Velkou and G.A. Gregoriou, Chem. Comm., 251 (1970); ibid., 1199 (1969).
4. (a) Ph.J. Dais, E. Souli and G.A. Gregoriou, data to be published shortly; (b) These azide ion activities (α) have been obtained (ref. 4a) as the product (5c) of sodium azide concentrations (total molality, m, of the azide ion, with no correction for any incomplete dissociation), times the corresponding azide ion activity coefficients (γ) in the particular aqueous dioxane medium considered (25 or 30%). These coefficients have been calculated from the values in water solution at 22°C (5d) by way of Harned's rule (4c); that is by multiplying the latter with the ratio of the activity coefficient of hydrogen chloride (of the same molality) in the aqueous dioxane medium (4d) over that in water (5b); (b) The azide ion activities so obtained for the values of the sodium azide concentrations given in ref. 2 are: (a, $[NaN_3]$): (25% Dioxane): 0.0505, 0.0758; 0.0709, 0.113; 0.0930, 0.156; 0.132, 0.237. (30% Dioxane): 0.0365, 0.0543; 0.0380, 0.0571; 0.0595, 0.0979; 0.0880, 0.152; 0.109, 0.199; 0.134, 0.258; 0.155, 0.311. These values have been used at 36.2°C neglecting the small temperature effect (5a) in going from 22 to 36.2°C; Any approximation involved in so obtaining the values of the activity coefficients can be neglected as it amounts to a small only percent error in comparison with the difference of these coefficients from unity; namely in comparison with the correction introduced by employing activities instead of concentrations. (c) H.S. Harned, J. Phys. Chem., 66, 589 (1962); (d) The activity coefficients of hydrogen chloride in 25 and 30% aqueous dioxane were obtained by interpolation from values for other aqueous dioxane compositions (4e) and for water (5b); (e) H.S. Harned and J.E. Donelson, J. Amer. Chem. Soc., 60, 339, 2128, 2133 (1938).
5. (a) S. Glasstone, "Introduction to Electrochemistry", D. Van Nostrand, Princeton, 1942; (b) Ibid. p. 139; (c) Ibid., p. 136; (d) E.A. Burns and F.D. Chang, J. Phys. Chem., 63, 1314 (1959).
6. R.A. Sneen and H.M. Robbins, J. Amer. Chem. Soc., 94, 7886 (1972).
7. Similar plots are also obtained by plotting the data vs. sodium azide activities.
8. (a) A closer examination suggests that these plots do not necessarily prove linear dependence on either concentrations or activities. Either plot could, e.g., be fitted also by a concave curve. This important question will be discussed elsewhere (8b); (b) Will be discussed after the work on the 2-octyl system is repeated and expanded.
9. (a) A more serious objection to such a test and conclusion is that it appears to provide information on activity coefficients (activities) — thermodynamic variables known and measurable from definitive evidence — by way of mechanistic information, such as the linearity of product plots, which can have more than one interpretation; (b) Another objection is the use of a conclusion — even if it were correct — drawn from product data, in the treatment of rate data. This is so because different rate and product determining steps, that could be involved, could, at least in principle, make use of different nucleophilic species.
10. It should be pointed out that linearity in the rate plots is obtained simply by a gradual up to about 20% (at the highest sodium azide concentration) non-proportionality between concentrations of salt and the actual nucleophilic species involved in the reaction. This is approximately (actually a little less than) what is also the result of using activities instead of concentrations. The lower absolute numbers representing activities are not necessary for, and without significance in, the arguments in this paper; they simply change the values of the slopes of the straight lines, and to the same extent for both the rate and product plots.
11. We are examining these systems as well, and expect to find that the between zero and first order apparent dependence of the reaction on anionic nucleophiles reflects primarily, but not necessarily in all cases, the curvature of the plot of activities of salts vs. their concentrations, rather than the proposed mechanistic scheme.
12. The k_{NA} values of ref. 2, obtained from the relation $k_{NA} = k^o (1 + b[salt])$, have been used here as such, without changing the values of $[NaN_3]$ into activities; this because the constant b had been calculated (2) experimentally from this relation itself by using concentrations ($LiClO_4$). Thus, when b is calculated by using activities of $LiClO_4$, and then used to calculate k_{NA} by using activities of sodium azide, these k_{NA} values are identical (within a difference of up to only 1.5%, totally insignificant compared to the experimental errors) to those of ref. 2. This is expected because of the similarity between the activity coefficients of $LiClO_4$ and NaN_3 (4a) in the concentration range of $LiClO_4$ used (ref. 2) to obtain the constant b.