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PRODUCTS AND THEIR SIGNIFICANCE IN THE SOLVOLYSIS OF 2-OCTYL METHANESULFONATE IN 30% AQUEOUS DIOXANE IN THE PRESENCE OF SODIUM AZIDE

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We have recently questioned[1,2] the evidence of Sneen and Larsen's study of the 2-octyl system[3] in support of the particular unification of solvolysis mechanisms proposed by Sneen,[3,4] and originally the alleged observation of a between zero and first order rate dependence on the nucleophile. Such a dependence is *required* by the proposed theory when a rate-product discrepancy is observed such as that reported for this system.[3] However, when we plotted Sneen and Larsen's data against azide ion *activity* ($\alpha_{N_3^-}$) instead of the *concentration* of sodium azide used in the initial study, as we suggested that they should, the original downwards curved rate plots were converted into linear ones.[1] This suggested a first order rate dependence, that is S_N2-like behavior. On the other hand, the rate-product discrepancy was of course maintained which suggested borderline behavior. This *combination* of conditions which is *incompatible* with Sneen's scheme disputed the conclusion that the reported data provided the evidence required and claimed in support of this theory.[1] At this point, it should be mentioned that other criticisms of Sneen's theory have also been published.[5,6]

The above argument would have been sufficient to prove our point, were it not for the linearity *claimed by Sneen and Larsen*[3] *for the product,* $[RN_3]/[ROH]$, *plot vs the concentration of sodium azide.* Similar linearities have been claimed in all of Sneen's work in support of the proposed unification.[3,4] Since linearities can hardly be fortuitous, this linearity coupled with the one of the product equation itself (eq 1) suggests, if real, that this concentration and not the activity is (whatever the reason) a correct or proportional measure of the nucleophile. We therefore examined Sneen's evidence for this linearity and found it inconclusive.[1] Furthermore, the following reasoning disputes the idea that plots against electrolyte *concentrations* can be linear (as often claimed). This reasoning is that the stoichiometric concentration of electrolytes should not be equal or proportional to either the concentration or to the activity of any of the species in solution, namely ions and ionized or nonionized electrolyte; *i.e.*, to any of the possible active species and measures of them. In support of this argument suffice for the time being to point out that there is ample evidence for only partial dissociation of even strong electrolytes and for lack of proportionality between their concentration and activity.[7] We, therefore, suggest that *plots against electro-*

TABLE I. Products in the Solvolysis of 2-Octyl Methanesulfonate[a] in 30% (V/V) Aqueous Dioxane at 39.0°

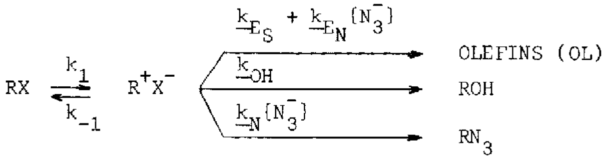
NaN_3[b]		N_3^-[b]	Products, mol %[c]			m[d]
m	M	α	Olefins	RN_3	ROH	
0	0	0	29.54 ± 0.47		70.46 ± 0.47	
0.02565	0.02615	0.01878	23.79 ± 0.60	21.01 ± 0.26	55.20 ± 0.59	14.56
0.05037	0.05134	0.03385	20.86 ± 0.37	33.81 ± 0.45	46.33 ± 0.43	14.21
0.1001	0.1021	0.06065	17.09 ± 0.25	47.10 ± 0.55	35.81 ± 0.39	12.88
0.1496	0.1524	0.08498	14.63 ± 0.31	55.60 ± 0.60	29.77 ± 0.64	12.26
0.2231	0.2268	0.1185	12.32 ± 0.33	63.58 ± 0.71	24.10 ± 0.67	11.63
0.3067	0.3110	0.1534	10.73 ± 0.31	69.03 ± 0.68	20.24 ± 0.56	10.97

[a] 0.00175m. [b] Solutions made up as molal, m (values corrected for consumption of azide). Corresponding molarities (M) experimentally determined. Activities ($\alpha_{N_3^-}$) calculated as before (1). [c] Products found stable to the reaction anf GC conditions. Their values, in relative percent (average absolute recovery 96%), are based on thirty GC determinations (from more than ten final experiments) for each NaN_3 concentration (8). Uncertainties are standard errors for a 95% confidence interval. [d] Constant of the equation 1, calculated using the *molarity* of NaN_3 for the term $[N_3^-]$.

lyte concentrations are not linear in the general case even if linear dependence on the active species is demanded by the reaction mechanism.

The above discussion points to the importance of a definitive answer to this linearity, both with respect to the specific issue of the evidence claimed for Sneen's theory as well as regarding the general question of a proper measure of eletrolytes. This answer is given in the present paper.

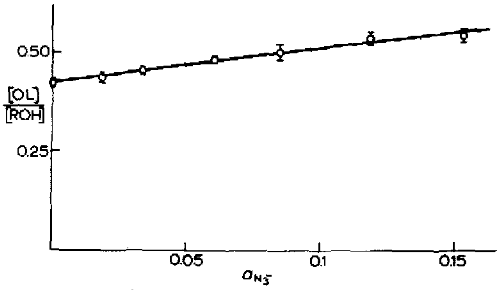
Following these considerations, we determined the products by GC analysis. This method, unlike Sneen's titrimetric one, made possible the differentiation between alcohol and olefin produced. The results (Table I) indicate a large olefin fraction[8] — 30% in the absence of sodium azide — as compared to the 0-2% reported or inferred in Sneen's[3] study and in McLennan's[6] recent reexamination of this solvolysis. Furthermore, the olefin to alcohol product ratio is not constant but increases with sodium azide and does so linearly with $\alpha_{N_3^-}$; a plot of [OL]/[ROH] *vs* $\alpha_{N_3^-}$ gives a fair linear fit (Fig 1). These findings suggest the following scheme and equations in terms of Sneen's theory and treatment:[3]



$$\frac{[RN_3]}{[ROH]} = m[N_3^-] \quad (1); \qquad \frac{[OL]}{[ROH]} = y + n[N_3^-] \quad (2); \qquad \frac{[RN_3]}{[ROH] + [OL]} = \frac{m[N_3^-]}{1 + y + n[N_3^-]} \quad (3);$$

$$\frac{k_{exptl}}{k_{NA}} = \frac{(1 + x + y)\{1 + y + (m + n)[N_3^-]\}}{(1 + y)\{1 + x + y + (m + n)[N_3^-]\}} \quad (4); \qquad \lim_{x\to\infty} \frac{k_{exptl}}{k_{NA}} = 1 + \frac{(m + n)}{(1 + y)}[N_3^-] \quad (5).$$

In these equations, which differ from those in the absence of olefin,[3,6] $x = k_{-1}/k_{OH}$, $y = k_{E_S}/k_{OH}$,



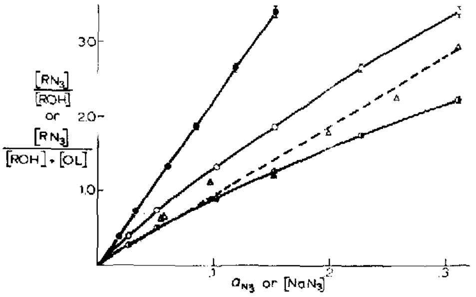


FIGURE 1(left). Plot of [OL]/[ROH] *vs* $\alpha_{N_3^-}$. The best linear fit drawn, described by $[OL]/[ROH] = y + n\,\alpha_{N_3^-}$ (eq 2'), has a correlation coefficient $r = 0.990$, a slope $n = 0.739$, and an intercept $y = 0.423$.
FIGURE 2(right). Plots of $[RN_3]/[ROH]$: (o—o), *vs* $[NaN_3]$; (●—●), *vs* $\alpha_{N_3^-}$, the best linear fit drawn (described by eq 1) has a correlation coefficient $r = 0.9999$ and a slope $m = 22.41$. Plots of $[RN_3]/([ROH]+[OL])$ *vs* $[NaN_3]$: (◐—◐), this study; (Δ--Δ), Sneen's data, (alleged to be of $[RN_3]/[ROH]$).

$n = k_{E_N}/k_{OH}$, $m = k_N/k_{OH}$, and k_{exptl} and k_{NA} are respectively the rate constants in the presence and absence of sodium azide, the latter corrected for salt effects.[3] These equations differentiate between borderline behavior (eq 4) and "S_N2-like" one (ion pair for $x \to \infty$ or *e.g.* true S_N2) (eq 5).[3,9]

We now turn to the main object of this study; namely the nature of the plot of $[RN_3]/[ROH]$ *vs* the *concentration* of sodium azide. Our data indicate that *this plot (Fig 2) is not linear as claimed,*[3] *but curved downwards!* Hence $[RN_3]/[ROH] \neq m[N_3^-]$ when the *concentration* of sodium azide is used for the term $[N_3^-]$! This is also reflected in the monotonous decrease of m with increasing sodium azide (Table I). On the other hand, the same plot against *azide ion activity* (Fig 2) *is linear*; that is $[RN_3]/[ROH] = m\,\alpha_{N_3^-}$ (eq 1'). Curved downwards *vs concentration* is also the plot of $[RN_3]/([ROH] + [OL])$, (Fig 2). The same plot in Sneen and Larsen's study, which was believed to be that of $[RN_3]/[ROH]$ since olefin was counted as alcohol, was concluded to be linear[3] and of higher slope (Fig 2).

These findings come in support of the aforementioned objections to linearities *vs* electrolyte *concentrations* and indicate that this activity, $\alpha_{N_3^-}$, and *not* the concentration of sodium azide is a good approximation to the proper measure of the active nucleophile; hence, the measure to be used in the rate plot as well for determining the order of this reaction. The latter can also be demonstrated mathematically: the term $m[N_3^-]$ in eqs 4 and 5 can be replaced by its equal $[RN_3]/[ROH]$ (eq 1), and this in turn by its experimentally proven equal term $m\,\alpha_{N_3^-}$ (eq 1'). Similarly, the term $n[N_3^-]$ can be replaced by $n\,\alpha_{N_3^-}$ (by way of eqs 2 and 2', Fig 1). Thus $[N_3^-]$ in eqs 4 and 5 is *also experimentally* required to be replaced by $\alpha_{N_3^-}$. The latter form of equations 4 and 5 dictates the use of this activity ($\alpha_{N_3^-}$) and not of the concentration of sodium azide in plotting the rate data, k_{exptl}/k_{NA}, in order to distinguish between the reaction order for borderline behavior (eq 4, downwards curved plot) and S_N2-like one (eq 5, linear plot). However, as we have already demonstrated,[1] when Sneen and Larsen's own k_{exptl}/k_{NA} data on this solvolysis are plotted against this activity, as now dictated that they should, they give a plot which is not curved downwards but is instead linear, *i.e.* in line with "S_N2-like" behavior; hence as now experimentally shown, Sneen and Larsen's *own* rate data do not support their conclusion of a between zero and first order dependence of the rate of this solvolysis on the nucleophile which is *one of the necessary* parts of the evidence for borderline behavior in Sneen's theory.[10]

In summary, the present study proves that the only among the data on this solvolysis[3,6] argued[3] to furnish evidence for Sneen's theory, namely those of Sneen and Larsen's[3] fail themselves to be compatible with one of the necessary parts of the alleged evidence. Additionally, and most significantly, this study offers a clean piece of experimental evidence pointing to some actual and potential misuses, having significant consequences, of the widely employed electrolyte *concentrations*. Furthermore, our study covers also most of the way for an independent and reliable answer to the question[1-6] whether this solvolysis under the conditions of Sneen and Larsen's study[3] obeys or not the criteria for borderline behavior of Sneen's theory. This it does: first by leading to the proper scheme and equations, secondly by providing dependable product data to be used also in a rate-product comparison,[9] and thirdly by establishing the proper measure of the nucleophile for determining the order of this reaction. This answer is given in the following communication.[9]

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6. (a) D.J. McLennan, *Tetrahedron Lett.*, 4689 (1975); (b) D.J. McLennan, *J.C.S. Perkin Trans. II*, 481, (1974); (c) The implications of our present findings (formation of olefin e.t.c.) on McLennan's work on the 2-octyl system (6a, b), and our reexamination of this author's initial study of this system (6b) will be discussed elsewhere.
7. (a) R.M. Fuoss and K.L. Hsia, *Proc. Nat. Acad. Sci.*, **57**, 1550 (1967); (b) Reference 1 and 2.
8. The olefin was identified as mainly 2-octene (richer in the *trans*- than in the *cis*-isomer) by comparison with authentic samples of octenes (1-, 2-, and 3-octenes) by CC (on *four* different columns), and by refractive index and nmr (after isolation by preparative GC).
9. G.A. Gregoriou, following communication.
10. This conclusion is supported still further if *our* salt effect value of $b = 0.15$ (2) is used instead of Sneen's $b = 1.04$. This would lead to smaller k_{NA} values — $k_{NA} = k_o(1 + b[salt])$ (3) — and thus higher values and rate of increase of k_{exptl}/k_{NA} with NaN_3. This would convert the already linear (1) — by the mere use of $\alpha_{N_3^-}$ instead of $[NaN_3]$ — rate plot of Sneen's k_{exptl}/k_{NA} data into an upwards curved one; *i.e.*, an impossible situation for Sneen's theory.