RATES IN THE SOLVOLYSIS OF 2-OCTYL METHANESULFONATE IN 30% AQUEOUS DIOXANE IN THE PRESENCE

OF SODIUM AZIDE AND THE QUESTION OF BORDERLINE BEHAVIOR
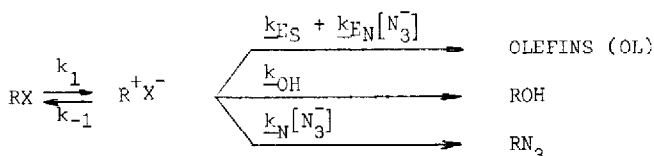
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Differences between a unification of solvolysis mechanisms proposed by Sneen[1] and our own "unified mechanism",[2] as well as our reservations[3-5] about some of the fundamental ideas and data which contributed to the arguments for this unification led us to a reexamination of the relevant work, and initially of Sneen and Larsen's study of the title solvolysis.[1a] Our reexamination of individual aspects of this solvolysis has justified these reservations and questioned[3-5] the evidence of the original study, but has not yet offered its own independent answer to the following question: does or does not this solvolysis under Sneen and Larsen's conditions, apart from these authors' data or arguments already questioned[3-6] or from other criticisms of Sneen's theory,[2a,7] offer the type of evidence claimed[1] for Sneen's theory? This answer is given in the present paper.

The scheme and some equations suggested[5] by our product findings in terms of Sneen's theory applied to this system are

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+X^- \Big\langle \begin{array}{l} \xrightarrow{\underline{k}_{ES} + \underline{k}_{EN}[N_3^-]} \text{OLEFINS (OL)} \\ \xrightarrow{\underline{k}_{OH}} \text{ROH} \\ \xrightarrow{\underline{k}_N[N_3^-]} RN_3 \end{array}$$

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

$$\frac{\underline{k}_{exptl}}{\underline{k}_{NA}} = \frac{1 + \underline{x} + \underline{y}}{1 + \underline{x} + \underline{y} + (\underline{m} + \underline{n})[N_3^-]} \left(1 + \frac{\underline{m} + \underline{n}}{1 + \underline{y}}[N_3^-]\right) \quad (3), \qquad \lim_{\underline{x} \to \infty} \frac{\underline{k}_{exptl}}{\underline{k}_{NA}} = 1 + \frac{\underline{m} + \underline{n}}{1 + \underline{y}}[N_3^-] \quad (4),$$

where $\underline{m} = \underline{k}_N/\underline{k}_{OH}$, $\underline{n} = \underline{k}_{EN}/\underline{k}_{OH}$, and $\underline{y} = \underline{k}_{ES}/\underline{k}_{OH}$ which are available experimentally from product distributions (eq 1 and 2); $\underline{x} = \underline{k}_{-1}/\underline{k}_{OH}$ is a constant independent of azide concentration; $\underline{k}_{exptl}$ and $\underline{k}_{NA}$ are respectively the rate constants in the presence and absence of sodium azide, the latter corrected for the salt effect component of the action of sodium azide;[1a] and $[N_3^-]$ stands for $\underline{\alpha}_{N_3^-}$ (azide ion activity) as shown.[5] Equations 1, 2, and 4 (the latter without the $\lim_{\underline{x} \to \infty}$) describe also a true S_N2 process (for the same scheme omitting the intermediate R^+X^-).

These equations differentiate between borderline behavior (eq 3) and "S_N2-like" one (ion pair for $\underline{x} \to \infty$ or e.g. true S_N2)(eq 4). In the latter case they predict a first order dependence of $\underline{k}_{exptl}/\underline{k}_{NA}$ on the nucleophile ($\underline{\alpha}_{N_3^-}$) and a rate-product correlation; namely an agreement between $\underline{k}_{exptl}/\underline{k}_{NA}$, obtained from rate data, and the right hand side of eq 4 calculated from product data (eq 1 and 2);

TABLE I. Rates, Azide Product Yields, and Comparison of Observed and Predicted Rate Constants, at 39.0°

NaN$_3$[a]		N$_3^{-}$[a]	k_{exptl} X 10^2,[b]	k_{S_N2} X 10^2,[c]	RN$_3$, mol%	
m	M	α	min^{-1}	min^{-1}	titrim.[d]	GC[e]
0	0	0	1.550 + 0.007	1.550	0	0
0.02635	0.02685	0.01929	2.000 + 0.014	2.047	19.0	21.50
0.05271	0.05368	0.03530	2.384 + 0.019	2.464	32.0	34.44
0.09734	0.09927	0.05920	3.009 + 0.022	3.094	44.2	46.50
0.1456	0.1483	0.08322	3.697 + 0.033	3.733	53.6	55.19
0.2178	0.2215	0.1163	4.629 + 0.030	4.627	61.4	63.16
0.2980	0.3023	0.1502	5.594 + 0.031	5.560	67.2	68.61

[a]Solutions made up as molal, m, (N$_3^{-}$ consumed during reaction was compensated for). Corresponding molarities (M) experimentally determined. Azide ion activity ($\alpha_{N_3^-}$) calculated as before (3). [b]Pseudo first order rate constants, determined by the pH-stat technique, represent each h the average of over eight rate constant determinations. Uncertainties are standard errors for a 9 % confidence interval. [c]Rate constants calculated from eq 4 (solved for k_{exptl}) with m = 22.41, n = 0.39, and y = 0.423 obtained from our product data (5), and k_{NA} calculated from Winstein's salt effect equation, k_{NA} = $k_0(1 + b[salt])$, (12), where k_0 = 1.550, [salt] = M_{NaN_3}, and b = b_{NaClO_4} = 0.5 (4). [d]Azide product based on the difference between infinity titers. [e]Azide product based on our GC data (5).

hence also a slope of the rate plot equal to (m + n)/(1 + y) (not equal to m as derived for the absence of olefin[1,6]). For borderline behavior (realistically 10>x>1/2),[1] these equations predict a between zero and first order dependence and a discrepancy from the above correlation; i.e., a "slope" (slope of the best linear fit) of the rate plot lower than the value of (m + n)/(1 + y) (see eq 3).[8]

Our k_{exptl} constants and titrimetric azide product yields are given in Table I. The latter yields compare well with those from our earlier GC data[5] (Table I). This insures against fortuitous gross errors in our two studies. The rate ratio k_{exptl}/k_{NA} is plotted in Figure 1 against both the concentration of sodium azide and azide ion activity. The correction for salt effects in calculating k_{NA} (Table I) has been based on the assumption that the salt effect component of the action of sodium azide can be approximated by the effect of sodium perchlorate.[4,9] Plotted also, for comparison, are Sneen's[1a] k_{exptl}/k_{NA} values. Our rate plot vs concentration is curved downwards, whereas that vs activity is linear; i.e. first order vs the same measure of the nucleophile, $\alpha_{N_3^-}$, which gave a linear product, [RN$_3$]/[ROH], plot as well.[5] These findings and the perfect fit of our plots prove that the rate dependence is first order and not between zero and first order as alleged,[1] except vs the wrong measure of the nucleophile namely the concentration of sodium azide; hence, this solvolysis does not meet the criterion of the rate order imposed by Sneen's theory for borderline behavior, but is instead in line with the rate order for "S$_N$2-like" behavior. Furthermore, these findings add support to our general objection[5] to linearities vs the concentration of electrolytes.

Let us now turn to the second basic criterion of Sneen's theory; viz., that of a rate-product discrepancy. The slope of our rate plot is 16.54 (Fig 1) as compared to the value of 16.27 calcu-
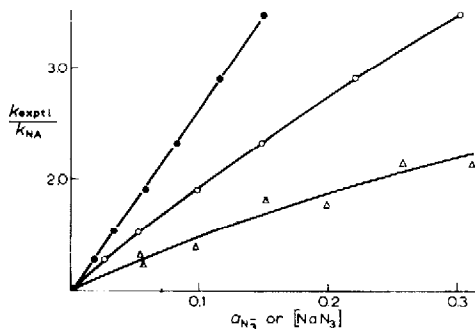
Figure 1. Plot of k_{exptl}/k_{NA}: o—o, vs $[NaN_3]$ (M); •—•, vs $a_{N_3^-}$, the best linear fit drawn has a slope 16.54 and a correlation coefficient $r=0.9996$. Plot of k_{exptl}/k_{NA} from Sneen's data (1a) vs $[NaN_3]$:△—△

lated for $(m + n)/(1 + y)$ from m, n, and y (Table I) obtained from our product data;[5] i.e. a perfect

agreement between the two sides of eq 4 (but not of eq 3, since no single and small value of x can

allow this);i.e., a perfect rate-product correlation, unlike the large rate-product discrepancy con-

cluded by Sneen.[1] The applicability of eq 4, illustrated above in the average over the overall con-

centration range studied, is also shown for each individual point by the agreement between each

k_{exptl} constant and the respective k_{S_N2} one calculated from this equation (Table I). Furthermore,

the fact that the average correlation lies within a spectacular 1.5% of the two values compared,

16.54 vs 16.27, which is not likely to be fortuitous attests also to the accuracy and reliability

of our present and earlier[4,5] work which is all reflected in this correlation.

The significance of the above findings is greatly enhanced by the fact that our study,[3-5] unlike

that of McLennan's[6] which is the only other experimental reexamination of this system, has referred

to the same original system and conditions as in Sneen and Larsen's study;[1a] and, furthermore, has

thoroughly treated the individual features of this solvolysis, including some of the principles in-

volved, which had contributed to the alleged evidence for borderline behavior. In so doing, our

study has also furnished the elements for an understanding of the causes for the opposite conclusion

reached in the original[1a] study. This should contribute greatly to answering objections and the

puzzling[7] question "how about the evidence for Sneen's scheme in the original study?" namely to an

answer which is essential before the issue raised around this solvolysis[1,2a,3-7] can be settled.

Some of these causes were Sneen and Larsen's "high" azide product yields, i.e. "high" $[RN_3]/([ROH] +$

$[OL])$ values,[5] and their "low" k_{exptl}/k_{NA} values (Fig 1).[10] These causes contributed additively to

the creation of the alleged rate-product discrepancy. Additionally, the use by these authors of the

concentration of sodium azide as the measure of the nucleophile was one of the factors, an other one

being their "high" salt effect value,[4] which contributed as already shown[4,5] to creating downwards

curvature in their rate plot, i.e. the alleged between zero and first order rate dependence.

The above proven failure of this system to obey both basic conditions imposed by Sneen's scheme for borderline behavior, and the evidence offered instead for "S_N2-like" behavior prove that this solvolysis in 30% dioxane does not furnish the evidence claimed[1] in support of this theory. On the other hand, no evidence against this theory itself either is provided by this failure — this solvolysis could be said not to be a borderline one in the sense of Sneen's scheme. However, the support for this mechanism is seriously weakened by our findings. The 2-octyl system in 30% and 25% dioxane has been the only truly secondary system among those which have been argued to obey the borderline kinetics of Sneen's scheme. Most of the other systems used,[1] although formally secondary, e.g. α-phenethyl, or even primary, e.g. p-methoxybenzyl, should be classified as roughly "tertiary" in terms of their ability for intramolecular nucleophilic contribution to the reacting carbon.[11] This suggests that if this solvolysis proves to behave as above in the 25% dioxane medium as well, then the generalization of Sneen's particular scheme to cover systems from tertiary to primary[1] would loose much of its principal support claimed; even if the evidence from some or all of these other systems studied were accepted.

The present findings recommend a reexamination of this solvolysis in the 25% aqueous dioxane medium also, as well as of some of the other systems used by Sneen in support of his theory.

REFERENCES and FOOTNOTES

1. (a) R.A. Sneen and J.W. Larsen, J. Amer. Chem. Soc., 91, 362 (1969); (b) R.A. Sneen, Accounts Chem. Res., 6, 46 (1973), and references cited therein; (c) R.A. Sneen, G.R. Felt, and W.C. Dickason, J. Amer. Chem. Soc., 95, 638 (1973).
2. (a) G.A. Gregoriou, Chim. Chron. (New Series), 3, 95 (1974); (b) S.L. Loukas, M.R. Velkou, and G.A. Gregoriou, Chem. Comm., 251 (1970); (c) 1962-1968 references to the present author's work cited in ref. 2a-b.
3. G.A. Gregoriou, Tetrahedron Lett., 233 (1974).
4. Ph.J. Dais and G.A. Gregoriou, Tetrahedron Lett., 3827 (1974).
5. G.A. Gregoriou, preceeding communication.
6. (a) D.J. McLennan, J.C.S. Perkin Trans. II, 481 (1974); (b) D.J. McLennan, Tetrahedron Lett., 4689 (1975); (c) The implications of our findings (olefin e.t.c.) on McLennan's study of the 2-octyl system (6a,b) and our reexamination of this author's first study (6a) will appear elsewhere.
7. (a) For references to some criticisms of Sneen's theory see ref 5. For reviews on this subject see e.g. ref 7b; (b) D.J. Raber, J.M. Harris, and P.v.R. Schleyer, in "Ions and Ion Pairs in Organic Reactions", Vol 2, M.Szwarc, Interscience, New York, N.Y., 1974, chap. 3; J.M. Harris, Progr. Phys. Org. Chem., 11, 89 (1974);I.P.Beletskaya,Russian Chemical Reviews, 44, 1067 (1975).
8. Eq 3 for borderline behavior is another form of eq 4 of ref 5 and results from the latter by division with $(1 + y)$. This form gives a clearer illustration of its prediction that the "slope" of its rate plot is lower than that of the plot in the "S_N2-like" case (eq 4 in this paper).
9. Salt effects in this system are very small (4), e.g. $b_{NaClO_4} = 0.15$, i.e. $k_{NA} \simeq k_0$; thus any approximation involved in assuming $b_{NaN_3} = b_{NaClO_4}$ in calculating k_{NA} (Table I) can introduce a small only, at the most, error in the k_{exptl}/k_{NA} values.
10. (a) Sneen and Larsen's low k_{exptl}/k_{NA} values are due in turn to two causes (which contribute about equally). These are: (a) their(1a) "low" rate accelerations — their $k_{exptl}/(k_{exptl})_0$ is 2.82 at 0.311 M (NaN₃) vs our value of 3.61 at 0.302 M (Table I) — and (b) their "high" salt effects, their $b = 1.04$ vs our $b = 0.15$ (4), which lead to "high" k_{NA} values (Table I);(b)Our use of 39° vs Sneen's 38.2° has an insignificant effect and does not account for these differences (own data).
11. A. Streitwieser, Jr., Chem. Rev., 56, 571 (1956), pp 613-615; Unpublished data of ours.
12. A.H. Fainberg and S. Winstein, J. Amer. Chem. Soc., 78, 2780 (1956).