SALT EFFECTS IN SOLVOLYSIS.   I.   SOME SALT EFFECTS IN THE SOLVOLYSIS

OF 2-OCTYL METHANESULFONATE IN 30% AQUEOUS DIOXANE

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Salt effects, following Winstein's classical work,[2a] have, except for special salt effects,

been accepted to be primarily linear in salt concentration (eq 1) and non-specific.[2,3] The non-

$$k = k^o(1 + \underline{b}\,[\text{salt}]) \tag{1}$$

specificity is in line with the approach to salt effects fundamentally as medium effects.[2a]

We predict that these assumptions should be basically inadequate,[4] and that critical reexamina-

tion of the widespread evidence used in their favor may actually discredit rather than support them.

This communication reexamines some salt effects in the title solvolysis[3] which illustrates the use

of these assumptions and the type of evidence which has provided continued support to them, as well

as some serious consequences of their use, e.g. the support offered to a proposed unification of

solvolysis mechanisms.[3] Our objections to some features of this unification[5] and to some special

aspects also of the reported salt effects[6] add further specific interest to the present study.

We will also mention, even though we do not agree with, the suggested possibility of a sizable

negative salt effect ($\underline{b}$ = -1) in this solvolysis,[7a] as well as the satisfactory but not defini-

tive arguments against it,[7b] which add further interest to a study of salt effects in this system.

Following these considerations, a careful redetermination of salt effects in the title solvo-

lysis was undertaken by using the same salts as in the earlier study[3] plus sodium perchlorate.[6c]

The results are given in the Table and plotted in Figures 1 and 2. These results, which are ave-

rages of a large number of rate constant determinations for most salt concentrations (Table) and

have standard errors of the order of only ±0.5%, allow the following discussion.

The rate plots against salt concentrations (Fig 1) are curved downwards! This is reflected also

in the decrease in the $\underline{b}$ values with increasing salt concentration (Table), and is amply illust-

rated for sodium bromide and nitrate. Sodium perchlorate hardly exhibits an effect, and the ef-

fect of the lithium salt is too small to allow detection of any curvature. Significantly, the same

rate plots against salt activities[9] (Fig 2) are linear![10b,11] These results lead to the important

conclusion that <u>salt effects are not linear in salt concentration and that eq 1 as defined does</u>

TABLE. Salt Effects in the Solvolysis of 2-Octyl Methanesulfonate[a] in 30% Aqueous Dioxane[b] at 43.5°

$\underline{M}$	NaBr			NaNO₃			LiClO₄		NaClO₄	
	$k \times 10^2$ min^{-1}[c]		$\underline{b}$[d]	$k \times 10^2$ min^{-1}[c]		$\underline{b}$[d]	$k \times 10^2$ min^{-1}[c]		$k \times 10^2$ min^{-1}[c]	
0	2.495 ± 0.009			2.379 ± 0.009			2.378 ± 0.009		2.478 ± 0.023	
0.0996	2.772 ± 0.011		1.11	2.517 ± 0.013		0.58	2.450 ± 0.004			
0.202	3.020 ± 0.013		1.04	2.630 ± 0.009		0.52	2.542 ± 0.015			
0.315	3.247 ± 0.024		0.96	2.736 ± 0.013		0.47	2.612 ± 0.009		2.598 ± 0.025	

[a] 0.0029 $\underline{M}$. [b] 30% (V/V), made up as 30.75% (W/W), (8). [c] Rates determined by the pH-stat technique. Rate constants represent the average of ten (NaBr), fifteen (NaNO₃), seven (LiClO₄), and eight (NaClO₄) rate constant determinations for each salt concentration and of the same number, as for each salt respectively, in the absence of salt. Uncertainties are standard errors for a 95% confidence interval. Rate measurements in the absence of salt were repeated in the study of each salt. [d] Calculated from eq 1 for the rate acceleration at each individual salt concentration. The corresponding $\underline{b}$' values (eq 2) are: For NaBr: 1.74, 1.78, 1.73. For NaNO₃: 0.95, 0.94, 0.93 (11).
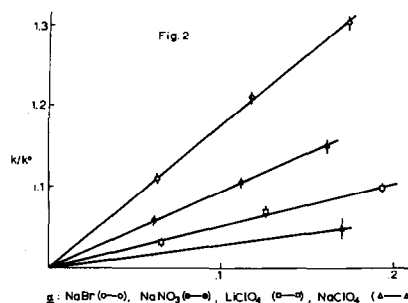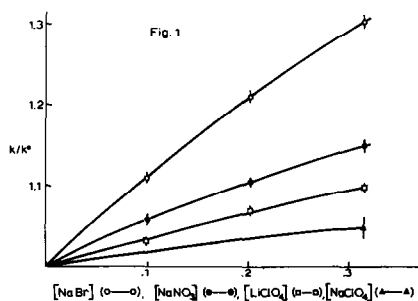
Figures 1 and 2. Plots of k/k^o vs salt concentrations, $\underline{M}$, (Fig 1), and salt activities, $\underline{a}$ (9), (Fig 2). Standard errors are indicated for each point. The $\underline{b}$ and $\underline{b}$'values (12), and the correlation coefficients, $\underline{r}$, of the plots against activities (Fig 2) are, (salt, $\underline{b}$, $\underline{b}$', $\underline{r}$): NaBr, 1.01, 1.75, 0.9998; NaNO₃, 0.51, 0.94, 0.9999; LiClO₄, 0.32, 0.52, 0.9978; NaClO₄, 0.15, 0.28.

not apply, at least in this case. They are also in line with the position[5] that the use of concentration as a measure of added electrolyte is unjustified.[10]

The magnitude of the observed salt effects is another most significant result. The $\underline{b}$' values — we define $\underline{b}$' by the equation (eq 2) $k = k^o(1 + \underline{b}'\underline{a}_{salt})$, where $\underline{a}$ is the activity of the salt—are 0.28, 0.52, 0.94, and 1.75 respectively for sodium perchlorate, lithium perchlorate, sodium nitrate, and sodium bromide.[11,12] The corresponding values of $\underline{b}$,[12] from eq 1 based on salt concentrations, are 0.15, 0.32, 0.51, and 1.01 as compared to the reported values[3] of 1.04, 0.73, and 0.73 for the last three salts respectively. The present results differ greatly, even their relative order is reversed, from the earlier values,[13] and indicate that all four salts exhibit small but still manyfold and substantially different salt effects! Furthermore, the effects of the three sodium salts increase in the order of the nucleophilicities of their anions.[14,15] An effect of the cation is also apparent; lithium perchlorate gives a larger effect than sodium perchlorate. Thus, unlike the earlier conclusions,[3] not only are these effects not similar to one another, but also,

as a result of this and of the above reactivity order, not all four effects nor that of lithium perchlorate can be used as a measure of the salt effect component of the action of sodium azide in this reaction. It is also clear that the best available approximation to a value for this compo-nent is that of sodium perchlorate; but then there is hardly an effect at all.[16,17] The $\underline{b}$ value is only 0.15 as against 1.04, the $\underline{b}$ value used earlier[3] for this salt effect component. Furthermore, this finding and the non-linear dependence of rates on salt concentration question still further[5] the validity of the rate plots, $k_{exptl}/k_{NA} \underline{vs} \left[N_3^-\right]$, of the earlier study of the title solvolysis,[3] and thus of the rationale on which a unification of solvolysis mechanisms was proposed.[18] This par-ticular example also illustrates potential pitfalls that ensue from the acceptance of eq. 1.

Most significantly, the present results are not in line with the medium effect nature of salt ef-fects,[2a] but agree with our theoretical considerations that include the suggested specific nature of salt effects.[4c] Surely, the case studied is too limited an example — it deals with a secondary system only, in a rather special solvent — to allow generalizations; nevertheless, it concerns be-havior observed in a highly aqueous and polar medium where specific effects should not be favored. Such results allow one to raise some basic questions about salt effects and solvolysis mechanisms, which are also raised in terms of our theoretical considerations.[4c] Some of them are: What is the significance of normal salt effects and the detailed role of salts in general? Which salt and why should be used to obtain a measure of this normal effect, or of the salt effect component of a nucleophilic salt? In fact, why should the k_{exptl} for such a salt be divided at all by the so-called normal salt effect,[3] or by what should it be divided, if by any, to give the inherent spe-cific effect of a nucleophilic salt? Answers to such questions will be given elsewhere in terms of our theory.[4c]

REFERENCES and FOOTNOTES

1.(a) Predoctoral fellow, 1973; (b) Author to whom inquiries should be directed.
2.(a) A.H. Fainberg and S. Winstein, J.Amer.Chem.Soc., 78, 2763. 2780 (1956), and other papers in the series; (b) C.L. Perrin and J. Pressing, ibid., 93, 5705 (1971).
3.(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).
4.(a) One reason for questioning the first assumption is that it rests on the use of the molar amount of added electrolyte as a measure of the latter, which has been suggested to be unjusti-fied (5,10b); (b) An answer to the question of linearity against salt concentrations (10b) would also assist in the choice between different interpretations of salt effects (2a,2b,4c); (c) The second assumption is questioned in terms of a "unified theory" to organic reactions (ref. 3 in ref. 5). According to this theory, salt effects are not expected to be mainly medium effects, but primarily specific effects on the reactants; moreover, they should not differ qualitatively from the effects of nucleophilic salts. All these effects should be basically similar in natu-re, and their magnitude should vary along a graded spectrum which at one extreme should blend with behavior apparently similar to such medium effects. This picture differs also from a recently proposed interpretation of salt effects in terms of a dipole-dipole interaction linear

salt effect model (2b).

5. G.A. Gregoriou, Tetrahedron Lett., 233 (1974).

6. (a) The scatter in the reported data (3a) does not allow a dependable discussion of the funda-
mental questions and alternatives involved (see e.g. ref. 5); (b) The extrapolation to a three-
fold higher concentration, 0.311 M, of the small effect of lithium perchlorate measured at
0.1 M (3a) cannot lead to a dependable value, even if the now questioned linearity of salt ef-
fects were applicable; and correct values of salt effects are most important in this case (see
text and ref. 18a); (c) Lithium perchlorate, used as a model for the salt effect component of
sodium azide (3a), is objectionable because it has a different cation which furthermore is no-
torious for its special properties (6d); (d) J.O.M. Bockris, Quart Rev., 3, 173 (1949); R.L.
Kay, J.Amer.Chem.Soc., 82, 2089 (1960).

7. (a) D.J. Raber, J.M. Harris, R.E. Hall, and P. v.R. Schleyer, J.Amer.Chem.Soc., 93, 4821 (1971);
these authors argue that the assumption of a negative salt effect having a b value of -1.0
would explain the results (3a) without necessary recourse to the proposed unification scheme;
(b) R.A. Sneen and H.M. Robbins, J.Amer.Chem.Soc., 94, 7868 (1972).

8. The same batch of 30% dioxane was used for the entire series of runs for each salt studied,
but three different batches were used respectively for sodium bromide, the two salts sodium
nitrate and lithium perchlorate, and sodium perchlorate. This fact accounts for the small
differences in the respective average rate constants in the absence of salt (Table), but does
not affect the salt effects — control experiments with sodium nitrate in these different
batches gave the same b' values.

9. (a) Salt activities in 30% dioxane, obtained as before (4b in 5) from the activity coeffici-
ents in water of NaBr (9b,d), NaNO$_3$ (9b,c,f), LiClO$_4$ (9b,e), and NaClO$_4$ (9b,e) are (salt, α
at: 0.0996, 0.202, 0.315 M): NaBr, 0.0631, 0.1176, 0.1751; NaNO$_3$, 0.0614, 0.1116, 0.1614;
LiClO$_4$, 0.0657, 0.1260, 0.1932; NaClO$_4$,0.0623, 0.1154, 0.1701; (b) R.A. Robinson and R.H.
Stokes, Trans.Far.Soc., 45, 612 (1949); (c) G. Scatchard, S.S. Prentis, and P.T. Jones,
J.Amer.Chem.Soc., 54, 2694 (1932); (d) ibid., 55, 4355 (1933); (e) ibid., 56, 807 (1934);
(f) E. Lange and A.L. Robinson, J.Physik.Chem., A148, 97 (1930).

10. (a) The present information supports this point — linearity is less likely to be due to for-
tuitous circumstances — but does not prove it, unless independent evidence were to show that
the mechanism of the action of salts demands linear and not curved rate dependence on them;
(b) The question of what should be the nature of rate plots against salts, as well as of what
is a proper measure of electrolytes will be discussed elsewhere.

11. The suggested use of b' values provides a true measure of salt effects, since any differences
resulting from differences in dissociation, or activity in general, are implicitly eliminated.
This provides for meaningful comparison of salt effects, unlike the usual comparison in terms
of b values. It is important to note also that the reported b' values do not vary with the
salt concentration and its range used — in line with, and reflected in, the linearity of the
plots against activities — whereas the b values do (Table). It should be, as will be discus-
sed elsewhere, that $\lim_{c \to 0} b = b'$!

12. These values of b and b' have been obtained as the slopes of the calculated best straight line
fits of the k/k^o data plotted against salt concentrations and activities respectively.

13. The small differences between the temperatures used in the two studies, 43.5^o vs 36.2^o, does
not affect the b values in any significant way, as deduced from control experiments (with NaBr).

14. K.M. Ibne-Rasa, J.Chem.Educ., 44, 89 (1967).

15. The possibility that these effects may not be "normal" salt effects as believed (3) and that
the salt anions may be involved in a nucleophilic displacement would not detract from, but
would enhance instead, the point (4c) by proving effects believed "normal" to be non-normal
and specific (see text, last paragraph).

16. (a) This finding parallels the essential lack of a salt effect by 2.0 M sodium perchlorate in
the solvolysis of 2-octyl methanesulfonate in 25% dioxane (16b). However, studies with such
high salt concentrations suffer from some drawbacks. This subject and some questions about
the work just published (16b) will be discussed in relation to our own work on the effects of
mixed salts, NaN$_3$ plus NaClO$_4$, in this system; (b) D.J. McLennan J.C.S.Perkin II, 481 (1974).

17. The results of this study give no indication of a negative salt effect of a b value of -1;
hence, they also suggest that the grounds on which the unification of solvolysis mechanisms
was proposed cannot be questioned in terms of such a salt effect (7a).

18. (a) The use of rate constants for the normal salt effect, k$_{NA}$, calculated by extrapolations to
higher salt concentrations with eq 1 (3), instead of the use of the increasingly lower than so
calculated real values of k$_{NA}$ suggested by the downwards curved salt effect plots demonstrated
in this paper, leads to increasingly lower than the correct k$_{expt1}$/k$_{NA}$ values. This converts
implicitly even a would be linear plot into a downwards curved one! The implications of this
point concerning the arguments in the earlier study (3) are obvious (5,18b); (b) This subject
will be discussed when the reexamination of this solvolysis (3a) has been completed.