JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 1, 359–362 (1988)

SHORT COMMUNICATION

THE SOLVATOCHROMIC EQUATION AND INSIGHT INTO CHEMICAL REACTIVITY

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SUMMARY

Reaction rates for solvolysis of a mustard analogue are accurately correlated by the solvatochromic equation without inclusion of a nucleophilicity term, and thus the equation is shown to reveal mechanistically significant information.

The Grunwald–Winstein and related approaches to prediction of solvent effects on rates have been found to be deficient for correlation of solvolysis rates of mustard derivatives.[1,2] Consequently we have examined the alternative approach of multiple linear regression analysis (MLRA). There has been a great deal of recent interest in application of MLRA to correlation of solvent effects on various chemical properties.[3] These include the solubility of nonelectrolytes[3,4] and electrolytes,[5] the distribution of solutes between water and various immiscible solvents,[3,6] and the effect of solvent on rotational isomerism,[3] keto–enol tautomerism,[3] and rate constants (as log k or $\Delta G^{\neq}$) for several chemical processes.[3,7–15] One of the most useful equations in MLRA is the 'solvatochromic' equation, equation 1, in which P is some property, $\pi_1{}^*$ is the solvent dipolarity/polarizability,[†] α_1 the solvent hydrogen-bonding acidity, β_1 the solvent hydrogen-bond basicity, and $\delta_H{}^2$ the solvent cohesive energy density.[13] The term in $\delta_H{}^2$ is the so-called 'cavity' term that takes account of the energy needed to create a hole or cavity in a solvent.

$$\log P = \log P_o + s\pi_1{}^* + a\alpha_1 + b\beta_1 + h\delta_H{}^2/100 \qquad (1)$$

Our interest here is to investigate the use of equation (1) to provide physical insight into the chemistry involved in a particular process, particularly with respect to reactivity. Thus in nucleophilic substitution reactions it has been suggested that the α term in equation (1) can be

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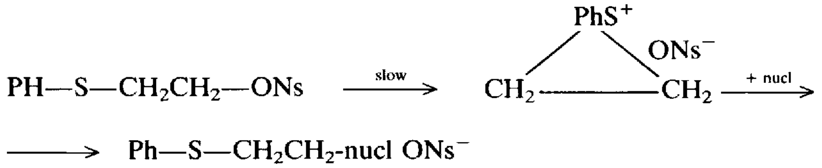
[†] For aromatic and polyhalogenated solvents, a polarizability correction term dδ is used in equation (1), but for the solvents used in this work δ = 0 and the term drops out of equation (1).

0894–3230/88/060359–04$05.00

Received 3 May 1988
Revised 5 July 1988

related to solvent electrophilicity (the ability to solvate an anionic leaving group) and that the β_1 term can be related to solvent nucleophilicity.[1,10,12–14] The *a* and *b* coefficients in equation (1) can then be taken as a measure of the sensitivity of a reaction to solvent electrophilicity and nucleophilicity. The goal of the present work is to test this proposal by determining the parameters required to correlate solvolytic reaction rates for a substrate that has been shown by other techniques to be insensitive to solvent nucleophilicity. If the correlation reveals a statistically significant *b* value, then we can conclude that the coefficients of the solvatochromic equation do *not* provide chemically meaningful information for this substrate. Alternatively, such a negative finding may allow one to conclude that β_1 is not a good measure of solvent nucleophilicity. On the other hand, the finding that *b* is statistically insignificant would provide support for the contention that equation (1) provides chemical insight into processes which are correlated by the equation.

We have chosen for this test the solvolysis of 2(phenylthio)ethyl 2-naphthalenesulfonate (-ONs) in various pure solvents, equation (2). Pure solvents are used to avoid complications from solvent sorting. We found that experimental scatter in rate constants was reduced when a small amount of 2,6-lutidine was added to the hydroxylic solvents and thiourea was added to the weakly nucleophilic, nonhydroxylic solvents. These additives did not change the rate constants. Possibly, the lutidine acts to scavenge acid and reduce side reactions, while thiourea traps the intermediate sulfonium ion thus preventing return and formation of potentially complicating products. Earlier work has clearly shown that the reaction of equation (2) proceeds by rate-determining neighboring sulfur participation to give the sulfonium intermediate, which is then rapidly captured by nucleophiles.[1,2,16–19] Only when powerful nucleophiles such as thiophenolate anions are used is S_N2 attack found.[18]



(2)

The kinetic results for reaction (2) at 25 °C in thirteen pure solvents in terms of $-\log k_1$ (s^{-1}) are: methanol, 3·57; ethanol, 3·86; 1-propanol, 4·10; 2-propanol, 4·20; 1-butanol, 4·22; ethylene glycol, 2·94; formamide, 2·44; trifluoroethanol, 1·78; dimethylformamide, 4·48; acetonitrile, 4·98; acetone, 5·16; dimethylsulfoxide, 3·81; and ethyl acetate, 5·58. Rates were determined by following disappearance of the sulfonate peak at 325 nm; errors were less than 5%. These particular solvents were chosen to provide a distribution of solvatochromic parameters.[13]

We have correlated these rate data with equation (1) in its full form and with various parameters removed. The statistical term we have used in deciding statistical significance is the T test (or confidence limit). As in the past,[13] we regard a confidence limit of less than 0·95 as indicative of statistical insignificance. In the present instance we have found that coefficients give T tests of better than 0·99 or less than 0·70, so that decisions regarding statistical significance are straightforward.

Correlation with the full, four-parameter solvatochromic equation gives a reasonable correlation coefficient (r = 0·980), with the following T tests: *h*, 0·219; *b*, 0·668; *s* & *a*, 0·999.

$$\begin{aligned}\log k = {} & (-8{\cdot}02 \pm 0{\cdot}60) + (3{\cdot}78 \pm 0{\cdot}74)\pi_1^* + (2{\cdot}20 \pm 0{\cdot}25)\alpha_1 \\ & + (0{\cdot}40 \pm 0{\cdot}39)\beta_1 - (0{\cdot}05 \pm 0{\cdot}18)\delta_H^2/100 \end{aligned} \tag{3}$$

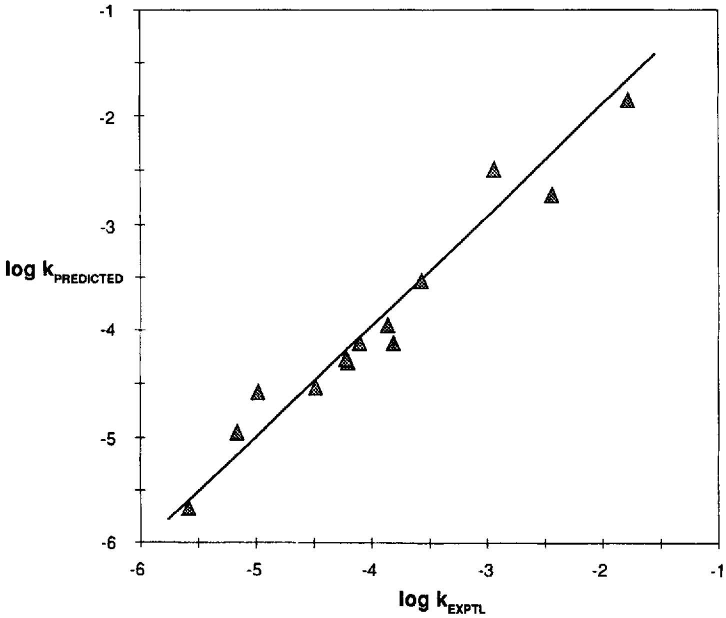


Figure 1. Plot of experimental log *k* values against those derived from the solvatochromic equation, equation (4), for solvolysis of 2-(phenylthio)ethyl 2-napthalenesulfonate

Similarly, correlation with a three-parameter equation containing α_1, β_1 and $\pi_1{}^*$ (note that k_o is also adjustable) gives a good fit again (r = 0·98), but still the T test for *b* (0·703) is far below the desired 95% level. Thus we conclude that there is no statistically significant dependence on δ_H or β_1.

Finally, correlation with only α_1 and $\pi_1{}^*$ gives a similarly good fit (r = 0·98, Figure 1), and dependencies on both parameters are statistically significant according to the T test (0·999 for $\pi_1{}^*$ and α_1), equation (4). Also, it is important that there is only a weak correlation between $\pi_1{}^*$ and α_1 ($r = -0{\cdot}26$).

$$\log k = (-7{\cdot}56 \pm 0{\cdot}32) + (3{\cdot}44 \pm 0{\cdot}39)\pi_1{}^* + (2{\cdot}12 \pm 0{\cdot}16)\alpha_1 \qquad (4)$$

It is also of interest that the *a* and *s* parameters for solvolysis of this mustard analogue are significantly smaller than the corresponding parameters for *t*-butyl chloride measured previously (a = 4·17 and s = 5·10);[13] presumably this indicates, as pointed out earlier,[19] that there is significantly less charge development in the transition state for solvolysis of 2-(phenylthio)ethyl-ONs, although it is possible that the charge development for the mustard analogue may be large but extensively delocalized. Finally, we note that the *a* value obtained from direct application of equation (1) for 2-(phenylthio)ethyl-ONs (2·12) compares favorably with the values of 2 and 1·6 for 2-(methylthio)ethyl chloride derived previously by approximate methods.[1]

In summary, rates for reaction (2) in thirteen pure solvents are correlated by the solvatochromic equation, in direct contrast to previous failures in attempts at correlation with the Grunwald–Winstein and related equations.[1,2] The correlation is found to be in accord with previous mechanistic observations; in particular, there is no dependence on solvent nucleophilicity as measured by β_1. Thus, as with the studies of *tert*-butyl chloride,[13] these experimental results support the contention that the solvatochromic equation provides physical insight into chemical reactivity.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the Army Research Office and the many helpful discussions of this work with M. J. Kamlet (to whose memory this work is dedicated).

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