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Reply to T. W. Bentley: Limitations of the *s*(*E*+*N*) and Related Equations**

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electrophilicity · kinetics ·
linear free-energy relationships · nucleophilicity ·
solvent effects

The preceding commentary[1] is the forth in a series[2–4] that tries to discredit our approach to a semiquantitative model of polar organic reactivity. None of these publications reports new experimental results, and all deal exclusively with a reinterpretation of our kinetic data. As the detailed analysis of the manifold mistakes and incorrect statements in references [1–4] would bore the nonspecialist reader, I will comment the most important points in this response and ask the interested reader to find my comprehensive reply in the Supporting Information, which also provides a detailed validation of the statements in this reply. Let me first explain the essence of the controversy, which is not described in reference [1].

The Patz–Mayr Approach

In recent years we have studied the kinetics of the reactions of carbocations and Michael acceptors with different types of nucleophiles, including alkenes, enol ethers, enamines, arenes, ylides, organometallic compounds, hydride donors, amines, phosphines, alcohols, alkoxides, and many more nucleophiles. The most commonly used solvents were dichloromethane, acetonitrile, DMSO, and water. The reactivities of electrophiles and nucleophiles thus studied cover a range of more than 30 orders of magnitude.[5] As bimolecular reactions in these solvents cannot be faster than 10^9–$10^{10}\,\mathrm{L\,mol^{-1}\,s^{-1}}$ (diffusion limit) and reactions slower than $10^{-5}\,\mathrm{L\,mol^{-1}\,s^{-1}}$ are difficult to measure, it is impossible to base a comprehensive nucleophilicity scale on measured rate constants for a single reference electrophile.

Therefore, we have defined a series of benzhydrylium ions and quinone methides as reference electrophiles, which differ widely in reactivity. We studied the kinetics of their reactions with various nucleophiles and performed a least-squares minimization on the basis of Equation (1).[7a,b] In this equation, electrophiles are characterized by one parameter (E), which we defined as solvent-independent, while nucleophiles are characterized by two parameters, the nucleophilicity parameter N and the nucleophile-specific sensitivity parameter s_N (previously termed s), which are treated as solvent-dependent. Fixed parameters were $E=0$ for $(4\text{-}\mathrm{MeOC_6H_4})_2\mathrm{CH^+}$ and $s_N = 1.0$ for 2-methyl-pent-1-ene.

$$\log k_{20^\circ\mathrm{C}} = s_\mathrm{N}(E+N) \qquad (1)$$

Reference [3] correctly describes that our basis correlation for deriving the reactivity parameters N, s_N, and E was based on 209 rate constants for the reactions of 38 π nucleophiles with 23 electrophiles in the reactivity range $-10 < E < 6$. It is not clear why Scheme 1 in both Ref. [4] and Ref. [1] now pretend that our basis correlation was restricted to electrophiles in the narrow range of $0 < E < 6$. This is not true![8] Details of our correlation are given in Appendix A of the Supporting Information.

Since both s_N and N are nucleophile-specific parameters, Equation (1) is equivalent to Equation (2), in which the nucleophilicity parameter Nu corresponds to $\log k$ of the reaction of the nucleophile in question with $(4\text{-}\mathrm{MeOC_6H_4})_2\mathrm{CH^+}$ [Eq. (3)].

$$\log k_{20^\circ\mathrm{C}} = s_\mathrm{N}E + Nu \qquad \text{with } Nu = s_\mathrm{N}N \qquad (2)$$

$$\text{for } E=0,\ \log k_{20^\circ\mathrm{C}} = Nu \qquad (3)$$

There are two reasons why we prefer Equation (1) over the mathematically equivalent, more easily understandable Equation (2):

1) As illustrated in Figure 1, the determination of the intercepts on the y axis (i.e., $Nu = s_N N = \log k$ for $E=0$) often requires long extrapolations, and Nu is an observable neither for very strong nucleophiles (reactivity is controlled by diffusion rate) nor for very weak nucleophiles (no reaction with $(4\text{-}\mathrm{MeOC_6H_4})_2\mathrm{CH^+}$).
2) The long extrapolations imply crossings of correlation lines with different slopes, with the consequence that the

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[**] I very much appreciate the invaluable help of Dr. Tanja Kanzian, Dipl.-Ing. Johannes Ammer, and Dr. Armin Ofial in preparing this reply. s = slope, E = electrophilicity, N = nucleophilicity.

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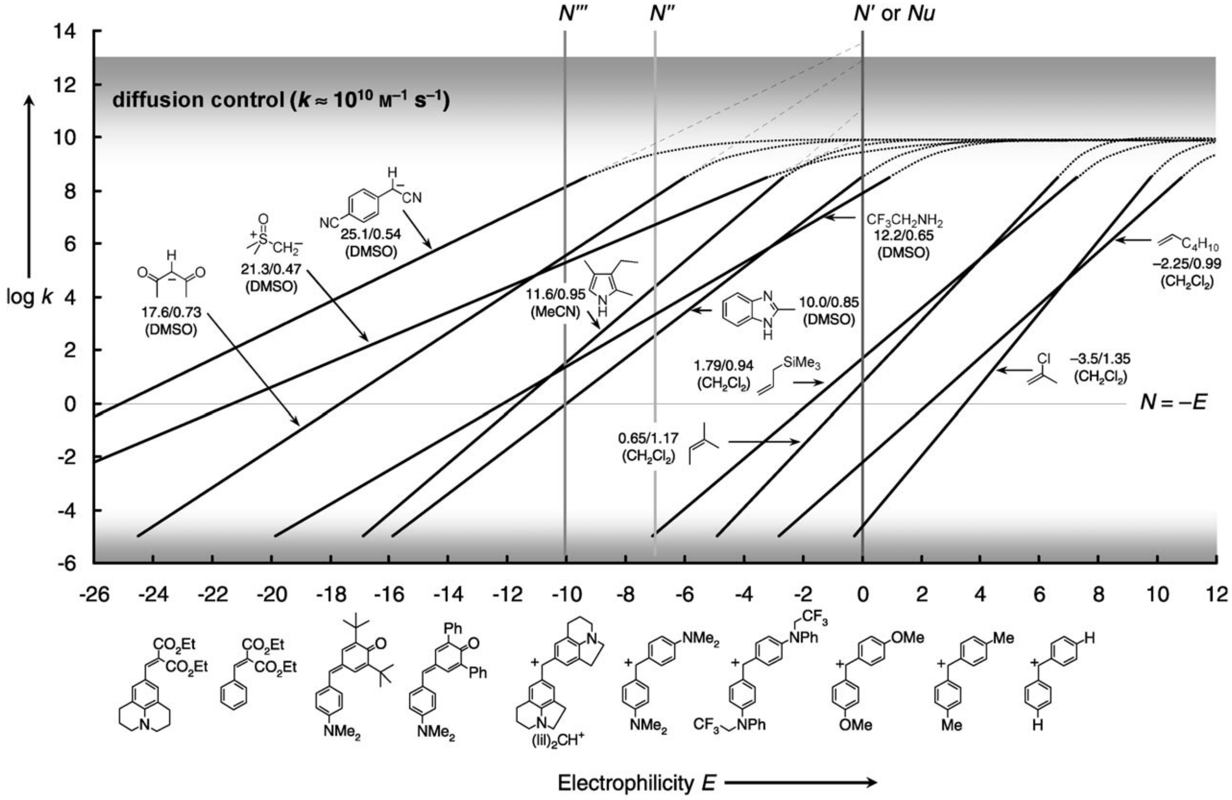

Figure 1. Rate constants for the reactions of nucleophiles with benzhydrylium ions, quinone methides, and arylidene malonates in different solvents at 20 °C. Nucleophilicity parameters N [Eq. (1)] are the intercepts on the abcissa; Nu [Eq. (2)], N' [Eq. (4)], N'' [Eq. (5)], and N''' [Eq. (6)] are the points of intersections of the correlation lines with the drawn vertical lines.[6]

> relative magnitudes of *Nu* of two nucleophiles often do not mirror their relative reactivities toward electrophiles that are actually used as reaction partners in synthetically employed reactions.

In contrast, Equation (1) defines nucleophilicity as the intercept of the correlation lines with the abscissa. The nucleophilicity parameter N thus equals the negative value of E of the electrophile that reacts with the nucleophile in question with a rate constant of 1 L mol^{-1} s^{-1} [$\log k = 0$ for $N = -E$; Eq. (1)]. As correctly stated by Bentley, we are using a floating reference scale. This is the price for having an undivided scale covering more than 30 orders of magnitude. Please note that this procedure is analogous to the Hammett acidity function method,[9] which has been used for positioning very strong and very weak acids on the same scale.

As the point of intersection of the correlation lines with the abscissa (Figure 1) is generally within or close to the experimentally accessible range, the determination of nucleophilicity N never requires long extrapolations, and it is the power of this approach that a first orientation on relative reactivities of nucleophiles and of electrophiles in synthetically useful reactions (usually $-5 < \log k < 9$) can be obtained by just looking at N and E scales without taking into account any sensitivity parameter s.

Bentley's Alternative

Instead of using one equation, Bentley splits up our correlation and so far has used three equations [Eqs. (4)–

$$\log k = E + s_E N' + c \quad \text{with } E = 0 \text{ and } s_E = 1.0 \text{ for } (4\text{-}MeOC_6H_4)_2CH^+ \tag{4}$$

(6)],[2–4] each of which was parameterized for a certain subgroup of reactions. Nucleophilicity is defined as log k for the reaction of a certain nucleophile with the corresponding reference electrophile (E or E'' or $E''' = 0$). Furthermore, he uses an electrophile-specific sensitivity parameter s_E (called s in Refs. [2,3]) instead of a nucleophile-specific sensitivity parameter s_N in our approach.

References [2,3] use Equation (4) for analyzing the reactions of benzhydrylium ions with solvents and with π systems. Different $(E+c)$ values are used in references [2,3] for the same carbocations. For many carbocations, even two different $(E+c)$ values are given in the same list, depending on the reaction partners used for the parameterization (see Table 3 in Ref. [3]), and the potential user does not know which one to select when trying to implement a new nucleophile.

Then, reference [3] introduces Equation (5) to correlate

$$\log k = E'' + s_E N'' + c \quad \text{with } E'' = 0 \text{ and } s_E = 1.0 \text{ for } (4\text{-}Me_2NC_6H_4)_2CH^+ \tag{5}$$

reactivities of more nucleophilic π systems. Again, different $(E''+c)$ values are used in Tables 6 and 8 of reference [3] for the same electrophiles in the same solvent. Which ones should be used for a new nucleophile?

Reference [4] continues to chop our large reactivity scheme into small pieces and creates an inflationary number of reactivity parameters, now for electrophiles and nucleophiles in DMSO [Eq. (6); for the definition of $(\text{lil})_2\text{CH}^+$, see Figure 1].

$$\log k = E''' + s_E N''' + c \qquad \text{with } E''' = 0 \text{ and } s_E = 1.0 \text{ for } (\text{lil})_2\text{CH}^+ \tag{6}$$

For most electrophiles there are two, in some cases even three, $(E'''+c)$ and s_E parameters presented in the same table (see Table 6 in Ref. [4]), depending on the reaction partners used for the parameterization.

Thus our single scale has been split up into three parts (actually four if footnote e from Table 1 in Ref. [3] is included), and the multiple parameters for a given compound make an unambiguous inclusion of new reagents impossible.

Number of Adjustable Parameters

One of Bentley's main arguments for the superiority of Equations (4)–(6) over Equation (1) is the use of fewer adjustable parameters in his approach. An example: reference [3] claims that Equation (5), corresponding to Equation (9) in reference [3], requires only 20 adjustable parameters to calculate 72 rate constants for the reactions of the 16 nucleophiles in Table 5 of reference [3] with the 11 electrophiles in Table 6 of reference [3]. How is this possible?

A tricky calculation: For one of the electrophiles (in this case $(4\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{CH}^+$) the value of $(E''+c)$ is set to zero, and the remaining 10 electrophiles give Bentley's 20 adjustable parameters (two for each electrophile). His counting does not include the N'' parameters for the 16 nucleophiles in Table 5 of reference [3], which are nothing but the logarithms of our measured rate constants with $(4\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{CH}^+$, which we published in Table 1 of reference [7a]. Unlike Bentley, we do not think that the rate constants with $(4\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{CH}^+$ are more reliable than others, and therefore we subjected them to the minimization procedure like the other rate constants. For that reason, Bentley counts them in our treatment as adjustable parameters; on the other hand, he defines the rate constants, which we measured with $(4\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{CH}^+$, as flawless and nonadjustable and thus gets to the small number of adjustable parameters in his treatment. A dubious practice, which is generally used in references [3,4].

Bentley's count of adjustable parameters fully ignores that he is using different E values in different solvents and that he is presenting up to three different E'' or E''' values for the same electrophile in the same solvent, depending on the reaction partners used for the correlation (see above). Furthermore, he is counting our parameters again and again for each of the fragmental correlations, ignoring the fact that they are the same in all correlations.

In our method, each electrophile is defined by one solvent-independent parameter (E), each nucleophile by two solvent-dependent parameters (N and s_N), and less than 1% of the parameters published since 2001 have needed revision to date.[7c] Why complain about a large number of adjustable parameters? Just use an honest count!

The Real Difference between the Two Approaches

Three of the articles in references [1–4] carry the term $s(N+E)$ in their title and severely argue against the floating reference scale associated with Equation (1). As pointed out above, Equation (2) is mathematically equivalent to Equation (1). Thus, if somebody feels uncomfortable with the use of a floating reference scale, she or he may as well employ Equation (2) to calculate $\log k$ from Nu $(=s_N N)$, E, and s_N. The calculated values of $\log k$ will be the same, and a person who is not interested in a qualitative interpretation of N can use the conventional correlation [Eq. (2)] just as well, in which nucleophilicity Nu fulfils Bentley's criterion for a clearly defined reference compound (that is, $\log k$ for the reaction of the nucleophile in question with $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^+$).

For that reason, Bentley's fight against "$s(E+N)$ and related equations" is improperly focused. The real difference between Equations (1) and (2) and Bentley's Equations (4)–(6) is that Equations (1) and (2) use a nucleophile-specific sensitivity parameter s_N, while Equations (4)–(6) use an electrophile-specific sensitivity parameter s_E.

Nucleophile- or Electrophile-Dependent Sensitivity Parameters

Figure 2,[10] which plots the same set of rate constants for the reactions of π nucleophiles with benzhydrylium ions in two different ways, explains why we introduced a nucleophile-specific sensitivity parameter. Only the graph in Figure 2a shows linear correlations (with different slopes s_N), while the plots in Figure 2b are not linear. Electrophile-specific sensitivity parameters s_E as suggested by Bentley cannot straighten the correlations in Figure 2b. The observation that 2-methyl-2-butene reacts faster with $(4\text{-MeC}_6\text{H}_4)_2\text{CH}^+$ than allyltrimethylsilane but more slowly with $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^+$ than allyltrimethylsilane cannot be corrected by an electrophile-specific sensitivity parameter. For that reason, poorer correlations are obtained when using Bentley's Equations (4) and (5) for reactions with π nucleophiles than with our Equation (1) (see below).

The manifold linear correlations which we have observed in plots of $\log k$ versus E for the reactions of various nucleophiles with benzhydrylium ions and structurally analogous quinone methides demonstrate that for these reactions, an electrophile-specific sensitivity parameter s_E is not needed. The situation is different when other types of electrophiles are used, for example $\text{S}_\text{N}2$ substrates.[11] In such cases, electrophile-specific sensitivity parameters s_E are important, as shown by Swain and Scott.[12] As discussed in reference [11], it depends on the type of reaction whether nucleophile-

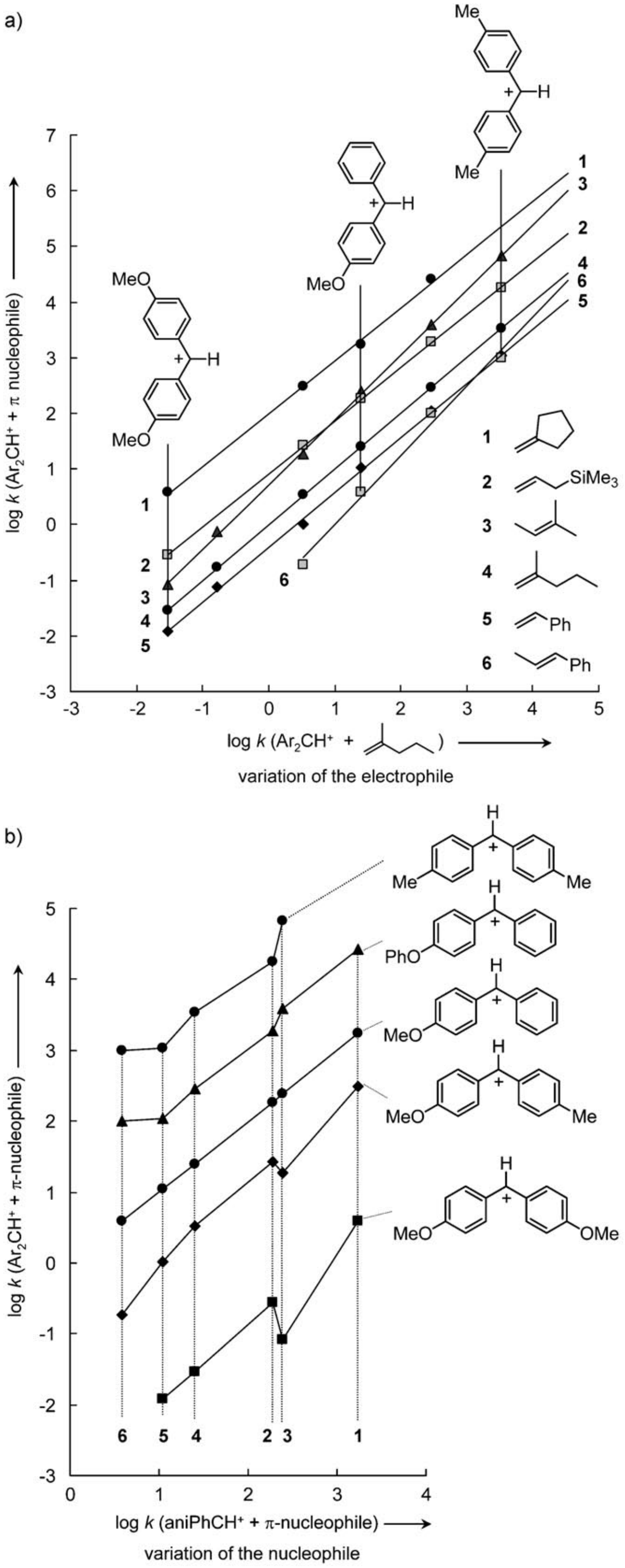

Figure 2. Plots of the rate constants (−70 °C, CH_2Cl_2) of the reactions of benzhydrylium ions with alkenes versus a) the reactivities of 2-methyl-1-pentene and b) the reactivities toward the 4-methoxybenzhydrylium ion (aniPhCH$^+$).[10]

specific (s_N, see Figure 2) or electrophile-specific sensitivity parameters (s_E) are needed (or both).

Reliability of Predictions

Bentley derives the "incorrectness" of Equation (1) from the fact that our N parameters deviate to different amounts from his N', N'', and N''' parameters, which he defines as correct. Analogously, he is criticizing that our E values differ from those which he considers as right.

However, most scientists will agree that the ability to make predictions of observables is a better criterion for the "correctness" or "incorrectness" of parameters than their agreement with Bentley's intuition. Therefore, we have calculated all experimentally available rate constants for the reactions of benzhydrylium ions with all nucleophiles listed in Tables 1, 5, and 7 of reference [3]. The results are unambiguous. As documented in detail in Tables S2 to S4 in Appendix B of the Supporting Information, in all cases the Patz–Mayr equation [Eq. (1)] gives much better agreement with the experimental rate constants than Bentley's equations [Eqs. (4) and (5)]. Most conspicuous are the results shown in Table S4 of the Supporting Information. While only five out of 175 rate constants calculated by Equation (1) deviate by more than 50 % from the experimental values, 54 of these 175 rate constants are outside this range when using Equation (5).[13] This fact is most remarkable, because Bentley's parameters have the advantage of being explicitly adjusted for the specific subsets of reactions, while the parameters in Equation (1) must hold for the whole set of data. The superiority of Equation (1) becomes even more evident when it is taken into account that reference [3] excluded several systems from the correlations (e.g. β-methylstyrene, 2-trimethylsiloxy-4,5-dihydrofuran) which are correctly treated by Equation (1). As discussed above, the poor performance of Equations (4) and (5) for these nucleophiles is due to their neglect of s_N.

Only when comparing nucleophiles with similar s_N parameters, as the alcoholic and aqueous solvents in reference [2], is the agreement between experimental and calculated rate constants somewhat better when using parameters that are specifically optimized for a certain group of reactions than when using the uncorrected E parameters derived from reactions of benzhydrylium ions with π nucleophiles in dichloromethane solution.

Solvent-Dependence of Electrophilicities

The only serious argument I can find in Bentley's papers is his concern about using solvent-independent E parameters. When applying Equation (1), we indeed employ the same E parameters for electrophiles in different solvents. This procedure is justified by the excellent correlations which we obtain when plotting rate constants (log k) determined in DMSO, water, acetonitrile, or other solvents versus E parameters derived from reactions in dichloromethane. As the reactions of most carbocations cannot be studied in

DMSO, and the reactions of most carbanions cannot be studied in dichloromethane, a change of solvent is inevitable. From the observation that the rate constants for the reactions of benzhydrylium ions with alkenes increase by less than a factor of five when changing from chloroform, dichloromethane, or dichloroethane to nitroethane or nitromethane solution, we had concluded, however, that solvent effects are within the noise level of our correlations.[14] Analogously, the rate constants for the reactions of PPh_3 with $(4\text{-}Me_2NC_6H_4)_2CH^+$ decrease by less than a factor of four when changing from dichloromethane to nitromethane, acetonitrile, acetone, or DMSO solution.[15]

The fact that the same E parameters can be used in different solvents does not mean, however, that all electrophiles are solvated to the same extent. By using the same values of E in different solvents, we just shift variable solvation of the electrophiles into the corresponding N and s parameters. This procedure is not uncommon. In the Hammett equation, for example, the substituent constants σ are assumed to be solvent- and temperature-independent, which also means that these effects are shifted into the reaction constant ρ. If the respective observables are calculated correctly, it does not matter which of the parameters include the solvation effects.

The good correlations obtained with the same E parameters of our reference electrophiles in different solvents do imply, however, that differential solvation is absent for these electrophiles, that is, that solvation changes linearly with electrophilicity E. Exceptions are known: Phenylamino-substituted benzhydrylium ions, for example, generally show small but constant deviations in the same direction when $\log k$ values for their reactions in acetonitrile are plotted against the E values determined in CH_2Cl_2.[16] These electrophiles show a slight differential solvation and will in the future be eliminated from the list of recommended reference electrophiles for the determination of the nucleophile-specific N and s_N parameters.

If it were not possible to use the same E parameters for the reference electrophiles in different solvents, it would be impossible to generate an undivided nucleophilicity scale, because there is not a single solvent that can be used for all types of reactions. This fact was eventually also realized by Bentley. We were pleased to see that after heavily attacking our use of the same E parameters in different solvents, he is doing the same on the last page of reference [4]: "*it appears that corrections for solvent effects in aprotic media will be relatively small, but not insignificant*". With this concession, Bentley also combined the different scales N', N'', and N''' to arrive at an unified N'' scale.

Please note, however, that Bentley's unified N'' scale of nucleophilicity in reference [4] equals $\log k$ for the reactions of nucleophiles with $(4\text{-}Me_2NC_6H_4)_2CH^+$. Therefore, it could have been calculated much more easily and much more precisely (see Appendix B in the Supporting Information) by Equation (1) from $E = -7.02$ and our published N and s_N parameters.

Reactivities of the N-Methyl-4-vinylpyridinium Ion

Presently we do not yet know which types of electrophiles require the use of solvent-dependent E and s_E parameters in certain solvents. In the criticized reference [17], we had explicitly mentioned that the reactions of the N-methyl-4-vinylpyridinium ion with amines do not follow Equation (1) and that the problem might be solved by introducing an electrophile-specific sensitivity parameter s_E. Because of that problem, we have abstained from calculating an E parameter for this electrophile. Instead of quoting our warning, Bentley himself used our Equation (1) to calculate the E parameter for this pyridinium ion in reference [1] and then demonstrated the incorrectness of the parameter which he, not we, had calculated.

I agree with Bentley that the correlation between $\log k$ of the reactions of amines with N-methyl-4-vinylpyridinium and $(4\text{-}Me_2NC_6H_4)_2CH^+$ (Figure 2 in Ref. [1]) is better than the corresponding $(\log k)/s$ versus N plot. This is not surprising: Correlations between two closely related reaction series are usually very good, because most factors which affect the rates of the two reaction series are the same.

What is the significance of the unity slope in this figure? Unfortunately, Bentley only discussed the correlation between the reactivities of amines toward the N-methyl-4-vinylpyridinium ion and $(4\text{-}Me_2NC_6H_4)_2CH^+$. Figure 1 in reference [1] shows that the slope is $s = 1.08$ when the reactivities of two benzhydrylium ions with $\Delta E = 3.0$ are correlated, and Appendix D of the Supporting Information shows an excellent correlation with a slope of $s = 1.19$ for the correlation of the reactivities of amines toward two benzhydrylium ions that differ by $\Delta E = 4.5$. Thus, these correlations do not generally have slopes of 1.0 (that is, constant selectivity relationships are not followed precisely), and the slope close to 1.0 shown in Figure 2 of reference [1] is entirely accidental. With other benzhydrylium ions as references, correlations with $s \neq 1.0$ would be found.

Bentley's reasoning that a single correlation with slope 1.03 proves that our equations are "incorrect" is indeed presumptuous. I recommend examining the "correctness" of any linear free-energy relationship, including the Hammett equation, in an analogous way!

Towards a General Scale of Nucleophilicity

Reference [1] criticizes that there is currently no satisfactory derivation of Equation (7), which we had demonstrated

$$\log k_{20^\circ\mathrm{C}} = s_N s_E (E + N) \tag{7}$$

to include Equation (1), the Ritchie equation,[18] and the Swain–Scott equation[12] as special cases.[11]

Linear free-energy relationships are empirical rules that describe relationships between rate constants or equilibrium constants. They can be interpreted but not derived. As shown in reference [11], simple algebra reveals the relationship between Equation (7) and the classical linear free-energy relationships (see also Appendix C in the Supporting Information).

Standard Reaction

There is one more correct statement in reference [1]: "*Arguably, one of the major problems associated with Equations (1) and (7)* [numbers adjusted] *is that there is no defined standard reaction; instead of calculating relative rates (log* k/k$_0$*), log* k *is obtained directly*". We are aware of the fact that calculating the logarithm of a quantity (number with unit) is not strictly correct. However, this formal inaccuracy is necessary to make the reactivity parameters E and N of immediate use for the synthetic chemist. Despite the fact that Bentley is right in this aspect, this criticism is remarkable, because it also applies to Bentley's Equations (4), (5), and (6). If Bentley is consistent and follows his own advice, he will now change all the equations in references [2–4] and replace $\log k$ by $\log k/k_0$.

Challenge to Theory

Reference [1] criticizes our statement in reference [5] that these correlations provide a challenge to theory. Please note the full statement (p. 586 in Ref. [5]): "*One referee raised the question whether linear free-energy relationships should work over such a wide range. As mentioned earlier, we are also astonished by these long linear ranges. The Leffler–Hammond effect should cause a downward bending and the frontier orbital effect should cause an upward bending as one moves from bottom left to top right in Figure 5* [corresponding to Figure 1 of this paper]. *We thus need two nonlinear effects which compensate each other to explain the long linear correlations. Not satisfactory! Theoreticians are challenged to provide a better explanation.*"

We still consider the long linearity of the log k versus E correlations, which we find again and again, as a challenge to theory. It should be noted that this amazing linearity is completely independent of the validity or nonvalidity of Equation (1). As E can be replaced by log k for the reactions of a series of carbocations with any nucleophile (see Figure 2a), it must be explained why log k versus log k correlations (i.e., correlations between directly measured rate constants) are linear in the range $-5 < \log k < 8$, and bending occurs only when $\log k > 8$, when the diffusion limit is approached. I repeat my appeal to theoreticians. There is a lack in our understanding of organic reactivity.[19]

Conclusion

Reference [1] states that "*Equation (1) was initially intended to be semi-quantitative (reliable to an order or two of magnitude), but confidence has grown to such an extent that many values of E and N are quoted to an accuracy of four significant figures.*"

It is true that our confidence in the wide applicability of Equation (1) has grown significantly in recent years, as we found that the reactivities of one class of nucleophiles after the other correlated linearly with the E parameters published in 2001 and 2002.[7] In this way, it has become possible to construct the most comprehensive nucleophilicity scale available to date.[7c]

Despite the increased confidence, we still consider Equation (1) as a semiquantitative approach to organic reactivity, and we have always mentioned a reliability of factor 10 to 100.[20] We have neither stated nor assumed that three or four parameters are sufficient for a reliable description of polar organic reactivity. Please note that the excellent agreement between experimental and calculated rate constants, which is discussed above, only holds for the reactions of nucleophiles with the reference electrophiles. In reactions with other electrophiles that are commonly used in synthesis, the deviations grow to factors of 10 to 100. This agreement is still remarkably good in view of the fact that an overall reactivity range of almost 40 orders of magnitude can be covered by using reference compounds which differ by more than 30 orders in reactivity. Despite these deviations, we usually publish E and N parameters with two decimals (please mind that they represent a logarithmic scale) to avoid unnecessary rounding errors when using these parameters for further correlations.

It is impossible to have both wide structural variability and high precision. This is our uncertainty principle! We have decided for the first option. If a traditional physical organic chemist is more interested in a closer look at narrow ranges of these correlations, that is fine with us. However, we cannot approve so-called improvements of the treatment of our kinetic data that first chop the comprehensive reactivity scales based on Equation (1) into small pieces, then confuse the reader by offering more than one "correct" reactivity parameter for a given compound and finally present correlations which give a much poorer agreement between calculated and experimental rate constants than ours. For these reasons, we reject Bentley's claim that his way of treating the kinetic data has proven the incorrectness of the correlation equations that we had introduced.

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[1] T. W. Bentley, *Angew. Chem.* **2011**, *123*, 3688–3691; *Angew. Chem. Int. Ed.* **2011**, *50*, 3608–3611.

[2] T. W. Bentley, *J. Phys. Org. Chem.* **2010**, *23*, 30–36.

[3] T. W. Bentley, *J. Phys. Org. Chem.* **2010**, *23*, 836–844.

[4] T. W. Bentley, *J. Phys. Org. Chem.* **2011**, *24*, 282–291.

[5] Most recent review: H. Mayr, A. R. Ofial, *J. Phys. Org. Chem.* **2008**, *21*, 584–595.

[6] In the case of N', N'', and N''' only the point of intersection corresponds to the indicated nucleophilicity parameter, but the correlation lines are different.

[7] a) H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, H. Schimmel, *J. Am. Chem. Soc.* **2001**, *123*, 9500–9512; b) R. Lucius, R. Loos, H. Mayr, *Angew. Chem.* **2002**, *114*, 97–102; *Angew. Chem. Int.*

Ed. **2002**, *41*, 91 – 95; c) For a database of reactivity parameters E, N, and s_N: www.cup.lmu.de/oc/mayr/DBintro.html.

[8] In his comment on my reply, Bentley requests to withdraw my statement “This is not true” with the argument that the Supporting Information of Ref. [7a] gives seven experimental rate constants for reactions of benzhydrylium ions with 2-methyl-pent-1-ene, for which $s_N = 1$. Table S20 of Ref. [7a] shows, however, that also for these reactions, calculated and experimental rate constants are not identical, that is, the rate constants of the reactions of seven benzhydrylium ions with 2-methyl-pent-1-ene were not used to define initial E values (as claimed by Bentley) and did not receive separate treatment. I have to repeat: Scheme 1 in both Ref. [4] and Ref. [1] are incorrect.

[9] L. P. Hammett, A. J. Deyrup, *J. Am. Chem. Soc.* **1932**, *54*, 2721 – 2739.

[10] Data taken from: H. Mayr, R. Schneider, U. Grabis, *J. Am. Chem. Soc.* **1990**, *112*, 4460 – 4467.

[11] T. B. Phan, M. Breugst, H. Mayr, *Angew. Chem.* **2006**, *118*, 3954 – 3959; *Angew. Chem. Int. Ed.* **2006**, *45*, 3869 – 3874.

[12] C. G. Swain, C. B. Scott, *J. Am. Chem. Soc.* **1953**, *75*, 141 – 147.

[13] In his comment on my response Bentley did not contradict this analysis but requested to mention that the rate constants calculated by his equations are also within the quoted errors. He furthermore requested to mention that “*he wrote in the conclusion to Ref. [3] that Mayr’s* E *values are obtained more directly and more precisely*”. Though I do not find this statement as clear in Ref. [3], I am grateful for this clarification because it more or less implies that Bentley’s “correct” N values do not have suitable counterparts (E values), which are needed for deriving observables ($\log k$).

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