Reactivities and selectivities of free and metal-coordinated carbocations

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Dedicated to Professor Wolfgang Steglich on the occasion of his 65th birthday.

Abstract - Most quantitative comparisons of carbocations, e.g. hydride affinities, heats of ionization, pK_{R^+} values, or solvolysis rate constants have been restricted to certain groups of compounds and do not allow the direct comparison of structurally different entities, for example ordinary carbenium ions, heteroaromatic cations, or cationic metal π-complexes. Such a comparison can be based on the kinetics of the reactions of these electrophiles with non-charged nucleophiles (e.g. π-systems, n-nucleophiles, or hydride donors). It is shown that the use of a floating scale of reference nucleophiles allows the development of a comprehensive electrophilicity scale (*E*-scale) which can be used for calculating absolute rate constants for the reactions of carbocations with a large variety of nucleophiles. The relationship of this electrophilicity scale with other "stability scales" is discussed.
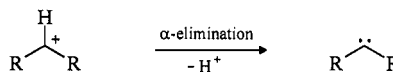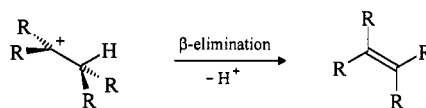
Introduction - Relationships between structures and stabilities or reactivities of carbocations have intrigued chemists for several decades (ref. 1). The desire to organize this information has led to various so-called stability scales, most of which have a well-defined physical basis (ref. 2). As shown in Scheme 1, these scales refer to two fundamentally different properties of carbocations, namely Brønsted or Lewis acidities. The category Brønsted acidity comprises protonation equilibria of arenes or alkenes [e.g. 1,1-diarylethylenes (ref. 3)] as well as the rates of the corresponding reactions (ref. 4). Lewis acidity related stability scales are based on the kinetics and thermodynamics of the formation and decay of Lewis acid-base adducts of carbocations with Lewis bases, as shown in Scheme 2.

From a theoretical point of view, hydride affinities (ref. 5) provide the most satisfactory comparison of carbocations since they refer to the gas phase and are undisturbed by solvation effects. While ICR and high pressure mass spectrometry as well as computations have provided hydride affinities for many small carbocations, there is a lack of data for synthetically important species, e.g. metal-coordinated entities.
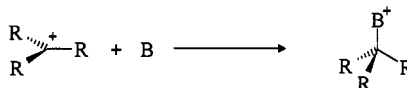
Arnett's heats of ionization of alkyl chlorides and alcohols in superacid media allow the direct comparison of a large variety of carbocations (ref. 6). Since the same conditions can be applied for

Scheme 1. Brønsted and Lewis Acidities of Carbocations

Brønsted Acidity

Lewis Acidity

generating secondary alkyl cations as well as highly stabilized species, systematic errors in the comparison of carbocations of widely differing stabilities are eliminated.

Scheme 2. "Stability-Scales" of Carbocations Based on Lewis Acid-Base Interactions

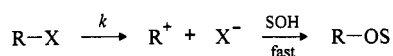Hydride affinities (gas phase data or computations)

$$R-H \longrightarrow R^+ + H^- \qquad \Delta_R H^\circ$$
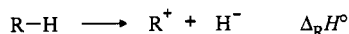
Heats of ionization in superacid solutions

$$R-Cl \xrightarrow[-50 \text{ to } -120^\circ C]{SbF_5/SO_2ClF} R^+ \qquad \Delta H_i$$

$$R-OH \xrightarrow[SO_2ClF, -40^\circ C]{SbF_5/HSO_3F} R^+ \qquad \Delta H_{rxn}$$
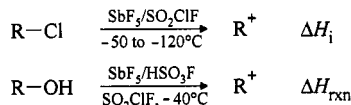
Equilibria in solution

$$R^+ + H_2O \underset{\Longleftarrow}{\overset{K_{R^+}}{\rightleftharpoons}} R-OH + H^+$$

$$R-X + R^+ \overset{K}{\rightleftharpoons} R^+ + R'-X$$
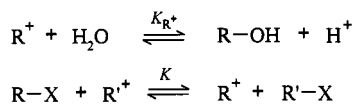
Solvolysis rates in weakly nucleophilic solvents

$$R-X \xrightarrow{k} R^+ + X^- \xrightarrow[fast]{SOH} R-OS$$

Rates of reactions with nucleophiles

$$R^+ + Nu \longrightarrow R-Nu^+$$
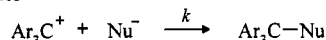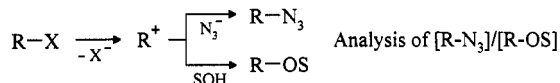
Scheme 3. Determination of the Electrophilic Reactivities of Carbocations

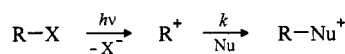Kinetics of the reactions of highly stabilized carbocations with anions and amines

$$Ar_3C^+ + Nu^- \xrightarrow{k} Ar_3C-Nu$$

C.D. Ritchie et al.

Competition experiments employing the azide clock

$$R-X \xrightarrow[-X^-]{} R^+ \begin{cases} \xrightarrow{N_3^-} R-N_3 \\ \xrightarrow[SOH]{} R-OS \end{cases} \quad \text{Analysis of } [R-N_3]/[R-OS]$$

W.P. Jencks et al., J.P. Richard et al.

Reactivities of laser-flash-photolytically generated carbocations

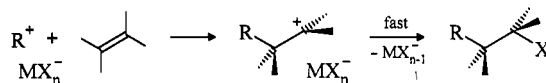$$R-X \xrightarrow[-X^-]{h\nu} R^+ \xrightarrow[Nu]{k} R-Nu^+$$

S. Steenken et al., R.A. McClelland et al., S. Kobayashi et al.

Kinetics of the reactions of cationic metal π-complexes with phosphanes and amines
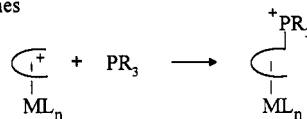
L.A.P. Kane-Maguire, D.A. Sweigart et al.

Kinetics of the reactions of carbocations and metal π-complexes with π-nucleophiles

H. Mayr et al.

However, due the low accuracy of the calorimetric method, the investigation of the effect of small structural changes is problematic.

Just the opposite is true for Deno's pK_{R^+} values (ref. 7). Since cations of similar Lewis acidity can be studied in media of similar acidity, one can reliably study the influence of small structural variations. On the other hand, comparisons of carbocations with different structures suffer from the known problems of the acidity function method (ref. 8). Furthermore, many carbocations with β-hydrogens behave as Brønsted acids, and the R^+/ROH equilibrium is usually not observable for alkyl substituted carbocations.

The most comprehensive set of data on carbocation stabilities can still be derived from the large body of kinetic investigations of solvolysis reactions in weakly nucleophilic media (refs. 1 & 9). Since rate constants referring to solvolyses in different solvents and compounds with different leaving groups are interconvertible by correlation equations (ref. 9), the major limitation of this method is the fact that highly stabilized carbocations do not form stable covalent esters, and therefore cannot be generated solvolytically.

In this contribution, we will focus on the reactions of carbocations with nucleophiles, i. e. the last topic listed in Scheme 2, and we will show that on this basis a reliable and comprehensive comparison of the reactivities of carbocations of different structure becomes possible.

Reactivity scales based on electrophilic reactivities of carbocations - The first systematic studies on the kinetics of the reactions of carbocations with nucleophiles were performed by Ritchie (ref. 10) who investigated reactions of highly stabilized carbocations, such as tritylium and tropylium ions, with anions and amines (Scheme 3). This work has largely been extended by Jencks and Richard (ref. 11) by introducing the azide-clock method which is based on the fact that many carbocations react with the azide ion with the known diffusion-controlled rate constant of 5×10^9 L mol^{-1} s^{-1} (ref. 12). Since this value is

independent of the nature of the carbocation, the product ratio $[RN_3]/[ROS]$ obtained by solvolysis of RX in azide solutions can be used to calculate the rate of the reaction of R^+ with the solvent SOH.

The laser-flash photolytic generation of carbocations in the presence of nucleophiles, which allows the direct determination of rate constants between approximately 10^6 L mol^{-1} s^{-1} and the diffusion limit, has been a major breakthrough in the investigation of these reactive intermediates (ref. 13).

It was the pioneering work of Kane-Maguire and Sweigart (ref. 14) which led to a characterization of the relative electrophilicities of a large variety of positively charged metal π-complexes. These authors had already included some aromatic π-systems in their studies (ref. 15), but most of the investigations on the kinetics of the reactions of carbocations with π-nucleophiles have been performed in our group (refs. 2 & 16).

Hosomi and Sakurai had already demonstrated that electrophilic alkylations of allylsilanes yield allylation products selectively (ref. 17) (Scheme 4). We could show that under certain conditions carbocation salts combine with ordinary alkenes to give [1:1] products exclusively (refs. 16a & 18). When studying the kinetics of these reactions, we observed that the relative reactivities of the π-systems

Scheme 4. Constant Selectivity Relationships of the Reactions of Benzhydryl Cations with π-Nucleophiles

depended little on the nature of the attacking electrophiles and that the relative reactivities of the carbenium ions depended little on the nature of the nucleophilic reaction partners (refs. 16a & 19).

Several hundred rate constants for the reactions of carbocations with nucleophiles have been determined by three independent methods and subjected to correlation analysis, and we reported that the whole body of data can be described by three parameters: one for the electrophiles (E) and two for the nucleophiles $(s$ and Nu or $N)$ (refs. 16b & 16c).

$$\lg k = Nu + sE \qquad\qquad\qquad (1)$$

$$\lg k = s(N + E) \qquad\qquad\qquad (2)$$

We have discussed previously that eq. (2) is equivalent to eq. (1) (refs. 16b & 16c), the conventional expression of a linear free enthalpy relationship (LFER). For practical reasons, it is preferable to use the nucleophilicity parameters N, as defined in eq. (2), and not the nucleophilicity parameters Nu in eq. (1). As one can see in Scheme 5, the intersections of the correlation lines with the ordinate (at $E = 0$), which define Nu, are often far remote from the range which is accessible by experiment. In these cases, the magnitude of Nu is strongly affected by small changes in s. In contrast, the N-values are obtained by the intersections of the correlation lines with the abscissa ($\lg k = 0$) which are usually within the experimental range. As a consequence, N depends little on s, and it is thus possible to base qualitative structure-nucleophilicity discussions on N without paying attention to s.

Since all reactions considered for these correlations involve combinations of cationic electrophiles with neutral nucleophiles, charge is neither created nor destroyed in the rate-determining step, and the reaction rates were found to depend little on solvent polarity (ref. 16b). Therefore solvent effects have been neglected in this analysis. For the sake of simplicity, also steric effects are not treated explicitly. Since the
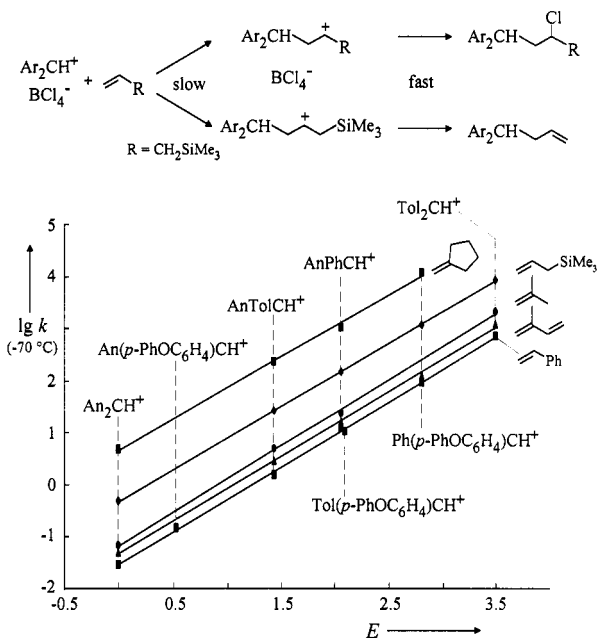
reactivity scales extend over 20 orders of magnitude, it is sufficient to predict rate constants with an accuracy of a factor of 10–100, and steric effects usually disappear in the noise of the correlations. This approximation becomes invalid if very bulky reagents are employed. For that reason tritylium ions and related compounds (ref. 20) are not included in these correlations. The electrophilicity scale derived from these correlations now provides comparisons of carbocation reactivities many of which are not accessible by other listings.

Scheme 5. Linear Free Enthalpy Relationships for the Reactions of Carbenium Ions with Nucleophiles
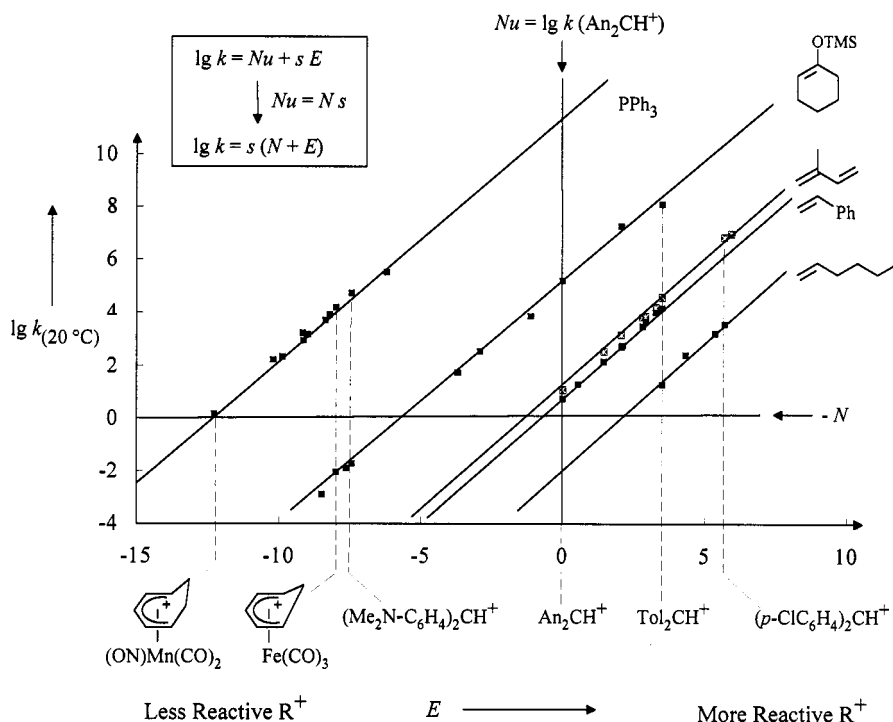

Electrophilicities of free and metal coordinated carbocations - Scheme 6 shows, for example, that α-methoxybenzyl cations (ref. 21) are slightly more reactive than the corresponding phenylogous benzhydryl cations (dashed lines). We recognize similar electrophilicities for the bis(p-anisyl)carbenium ion, the xanthylium ion and the hexacarbonyldicobalt-coordinated propargyl cations (ref. 22). Most remarkably, the reactivities of the latter species are hardly affected when the propargylic hydrogens are replaced by phenyl or other substituents, but a dramatic decrease of electrophilicity (by a factor of 10^5) is observed, when one of the carbonyl groups is replaced by the triphenylphosphane ligand (ref. 22).

Analogously, only a small reduction in reactivity is observed when one of the hydrogens in the ferrocenylmethylium ion is replaced by a phenyl group (ref. 23).

The tropylium ion is located in between the 1,3-dithienium ion and the 2-phenyl-1,3-dithienium ion (ref. 24), and it is interesting to see that the bis(p-dimethylamino)benzhydryl cation (ref. 25), the N-methylacridinium ion (ref. 26) and the tricarbonyliron-coordinated cyclohexadienylium ion (ref. 27) – representatives of three different classes of carbocations – show identical reactivities towards numerous types of nucleophiles.

We have previously discussed that these electrophilicity parameters can advantageously be combined with nucleophilicity parameters to predict which of these electrophile-nucleophile combinations are to be expected at room temperature (refs. 16b & 16c), thus providing a useful guide for planning organic and organometallic syntheses (refs. 16b, 16c, 22, 23, 25b & 28).

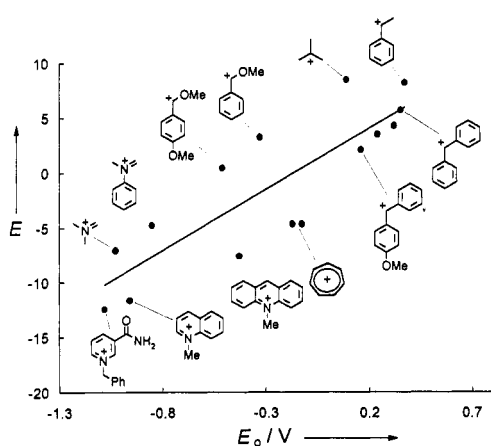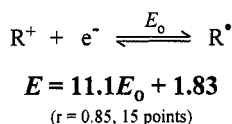Scheme 6. Electrophilicity Parameters E of Carbocations and Related Compounds
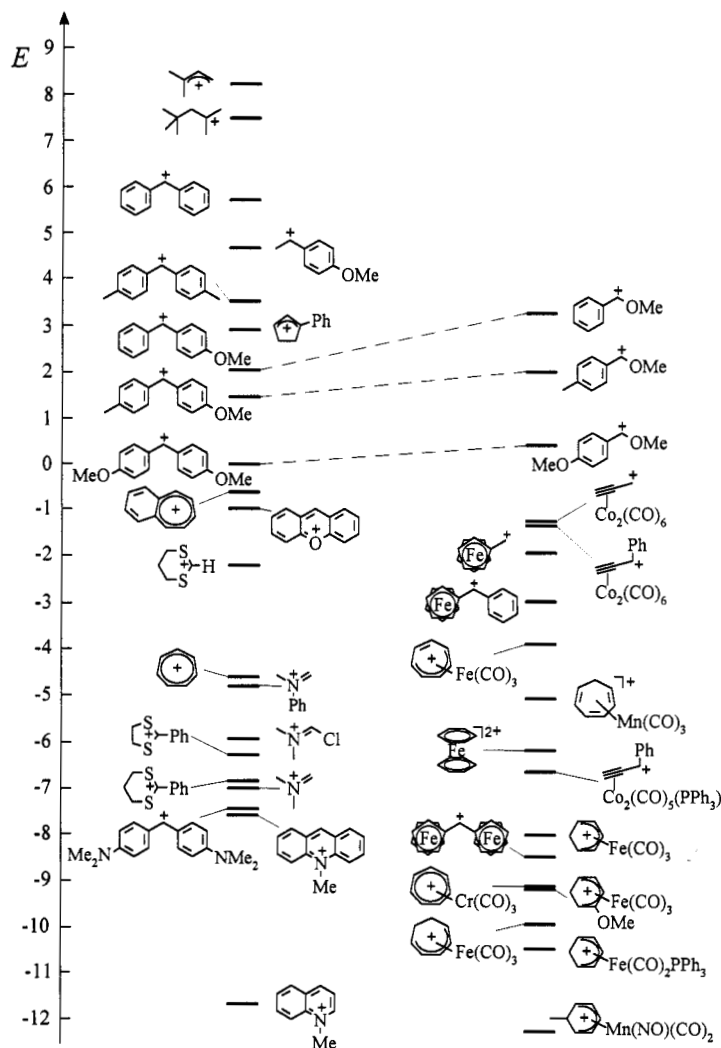
Correlations of the E parameters with other properties of carbocations - We will now turn to the question, what is behind these electrophilicity parameters? And how can we predict additional E-parameters from available literature data without performing additional experiments?

During the formation of a Lewis acid-base adduct, the carbenium ion accepts electrons (ref. 29), and one might expect a correlation of the electrophilicity parameters E with the reduction potentials E_0 (ref. 30). Scheme 7 shows that a weak correlation exists, but from the large spread of the individual points it is obvious that the driving force of the electron transfer is not the sole factor determining electrophilicity. Inspection of Scheme 7 shows that for a reduction potential of 0.4 V one might find E-parameters between +1 and −7 corresponding to a rate ratio of 100 millions, i.e., the reduction potentials may be employed for a first guess of electrophilic reactivity, but certainly a reliable prediction of electrophilicities from reduction potentials is impossible.

A much better correlation is shown in Scheme 8, which relates the kinetics of the formation of the Lewis acid-base adducts (E-parameter) with the thermodynamics of the reactions of the Lewis acids R$^+$ with the Lewis base OH$^-$ (pK_{R^+}). The error in E derived from pK_{R^+} is usually smaller than ±2. Since pK_{R^+} values for many stabilized carbocations, especially heteroaromatic cations (ref. 31), are available, this

correlation provides a good estimate for such electrophiles. It should be mentioned, however, that this correlation should not be employed for deriving *E*-values of highly reactive carbocations, e.g. the 1-arylethyl cations or cumyl cations, since their pK_{R^+} values are not accessible by equilibrium studies and have often been determined indirectly, e.g. from kinetic data (ref. 32). In such cases it is more straightforward to derive *E* directly from the corresponding rate constants instead of taking the detour via pK_{R^+}.

Scheme 7. Correlation of the Electrophilicity Parameters *E* of Carbocations with their Reduction Potential E_0
(vs SCE in MeCN, 25 °C)

$$R^+ + e^- \xrightleftharpoons{E_0} R^\bullet$$

$$E = 11.1 E_0 + 1.83$$

(r = 0.85, 15 points)

Scheme 8. Correlation of the Electrophilicity Parameters *E* of Carbocations with their Lewis Acidities pK_{R^+}

$$R^+ + H_2O \xrightleftharpoons{pK_{R^+}} R\text{-}OH + H^+$$

$$E = -0.630\ pK_{R^+} - 2.66$$

(r = 0.98, 35 points)
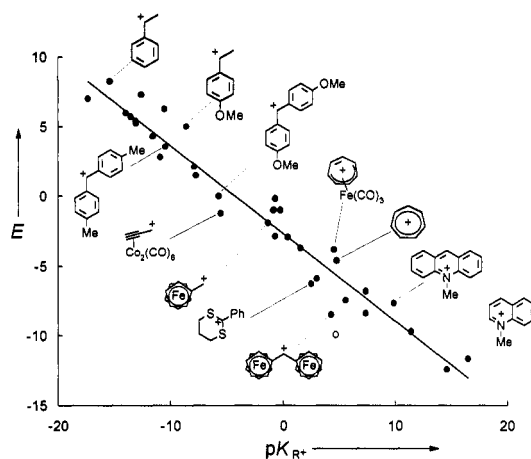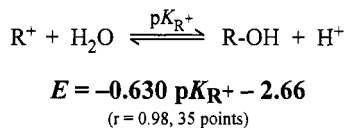
Scheme 9 shows a correlation of comparable quality between the electrophilicity parameters *E* and the ethanolysis rate constants lg k_{solv} (ref. 33). As expected, those carbocations which are produced most quickly in the solvolysis reactions are the least reactive ones toward nucleophiles. It should be noted, however, that this correlation does not hold for vinyl cations and related species where the rate-determining step involves the rehybridization of an sp^2 into a sp carbon.

Since in most cases carbon nucleophiles have been used for deriving the electrophilicity parameters *E*, methyl anion affinities appeared to be the most suitable thermodynamic data for the correlation with *E*. Scheme 10 shows a fair correlation of the *E*-parameters and the calculated [AM1 (ref. 34)] methyl anion affinities, the slope of which, when multiplied by $2.303RT$, is almost identical to that of the correlation of *E* and pK_{R^+} (Scheme 8). Though the iminium ions and the *N*-benzyl NAD$^+$ cation deviate and have not been used for the calculation of the correlation line, Scheme 10 indicates that electrophilic reactivities can now easily be obtained from quantum chemical calculations. Since *N*- and *s*-parameters have become available for representatives of most nucleophilic reaction partners (refs. 16b, 16c, 25b, 28c & 35), there is now a simple approach to approximate absolute rate constants for this class of reactions.

In principle, such rate constants should also be accessible by quantum chemical calculations of the corresponding transition states. Apart from the more complicated way of calculating non-minimum structures, an additional problem arises from the fact that many of these reactions are predominantly
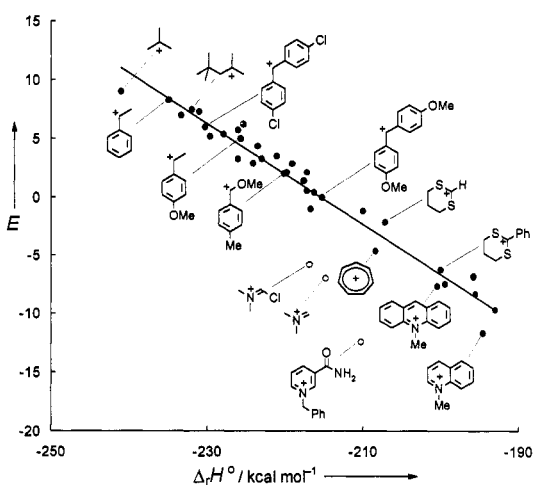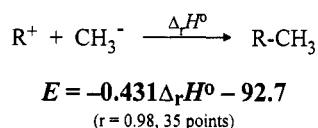
controlled by entropy instead of enthalpy (ref. 36). Though not diffusion controlled, such reactions do not have a barrier on the potential energy surface (ref. 36).

We, therefore, consider quantum chemical calculations of reaction enthalpies in combination with linear free enthalpy relationships as shown in Scheme 10 and eq. (2) to be presently the most efficient way to predict rate constants for the reactions of carbocations with nucleophiles.

Scheme 9. Correlation of the Electrophilicity Parameters E of Carbocations with the Ethanolysis Rate Constants of the Corresponding Alkyl Chlorides
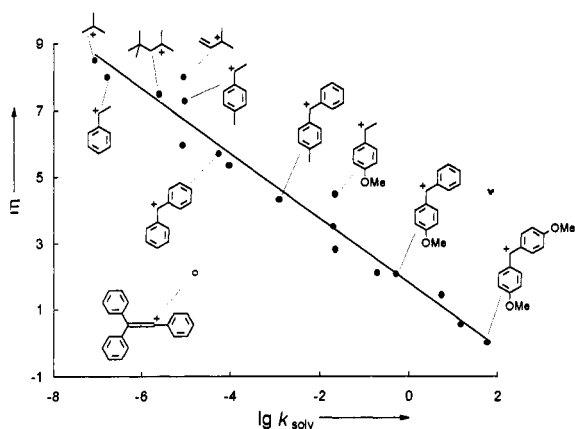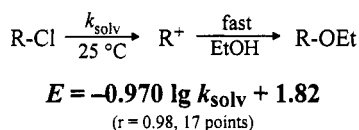
Scheme 10. Correlation of the Electrophilicity Parameters E of Carbocations with their Calculated (AM1) Methyl Anion Affinities ($-\Delta_r H^o$)

$$R\text{-}Cl \xrightarrow[25\,^{\circ}C]{k_{solv}} R^+ \xrightarrow[EtOH]{fast} R\text{-}OEt$$

$$E = -0.970 \lg k_{solv} + 1.82$$
(r = 0.98, 17 points)

$$R^+ + CH_3^- \xrightarrow{\Delta_r H^o} R\text{-}CH_3$$

$$E = -0.431\Delta_r H^o - 92.7$$
(r = 0.98, 35 points)

with $\Delta_f H^o(CH_3^-) = 33.4$ kcal mol^{-1} (from ref. 5b).

References
1. a) *Carbonium Ions* (G. A. Olah, P. v. R. Schleyer, eds.), Vol. I–V. Wiley-Interscience, New York (1968–1976). b) P. Vogel. *Carbocation Chemistry*. Elsevier, Amsterdam (1985). c) *Advances in Carbocation Chemistry* (X. Creary, ed.), Vol. 1. JAI Press, Greenwich CT (1989). d) *Advances in Carbocation Chemistry* (J. M. Coxon, ed.), Vol. 2. JAI Press, Greenwich CT (1995). e) *Stable Carbocation Chemistry* (G. K. S. Prakash, P. v. R. Schleyer, eds.). Wiley-Interscience, New York (1997).
2. H. Mayr. In *Cationic Polymerizations: Mechanisms, Synthesis and Applications* (K. Matyjaszewski, ed.), pp. 51–136. Marcel Dekker, New York (1996).
3. a) D. M. Brouwer, E. L. Mackor, C. McLean. In *Carbonium Ions* (G. A. Olah, P. v. R. Schleyer, eds.), Vol. II, pp. 837–897. Wiley-Interscience, New York (1970). b) R. Stewart. In *Organic Chemistry—A Series of Monographs* (H. H. Wasserman, ed.), Vol. 46. Academic Press, Orlando (1985).
4. a) K. Oyama, T. T. Tidwell. *J. Am. Chem. Soc.* 98, 947–951 (1976). b) W. K. Chwang, P. Knittel, K. M. Koshy, T. T. Tidwell. *J. Am. Chem. Soc.* 99, 3395–3401 (1977). c) P. Knittel, T. T. Tidwell. *J. Am. Chem. Soc.* 99, 3408–3414 (1977). d) W. K. Chwang, V. J. Nowlan, T. T. Tidwell. *J. Am. Chem. Soc.* 99, 7233–7238 (1977). e) V. J. Nowlan, T. T. Tidwell. *Acc. Chem. Res.* 10, 252–258 (1977). f) J. L. Jensen, V. Uaprasert. *J. Org. Chem.* 41, 649–654 (1976). g) R. Taylor. *Electrophilic Aromatic Substitution*. Wiley, Chichester (1990).
5. a) D. H. Aue, M. T. Bowers. In *Gas Phase Ion Chemistry* (M. T. Bowers, ed.), Vol. 2, Chapter 9. Academic Press, New York (1979). b) S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard. *J. Phys. Chem. Ref. Data* 17, Supplement 1 (1988).

6. a) E. M. Arnett, C. Petro. *J. Am. Chem. Soc.* 100, 2563–2564 (1978). b) E. M. Arnett, C. Petro. *J. Am. Chem. Soc.* 100, 5408–5416 (1978). c) E. M. Arnett, T. C. Hofelich. *J. Am. Chem. Soc.* 105, 2889–2895 (1983).

7. a) N. C. Deno, J. J. Jaruzelski, A. Schriesheim. *J. Am. Chem. Soc.* 77, 3044–3051 (1955). b) N. C. Deno, A. Schriesheim. *J. Am. Chem. Soc.* 77, 3051–3054 (1955). c) N. C. Deno, W. L. Evans. *J. Am. Chem. Soc.* 79, 5804–5807 (1957).

8. a) A. Bagno, G. Scorrano, R. A. More O'Ferrall. *Rev. Chem. Intermed.* 7, 313–352 (1987). b) M. Liler. In *Organic Chemistry–A Series of Monographs* (A. T. Blomquist, ed.), Vol. 23. Academic Press, London (1971). c) J. Hine. *Structural Effects on Equilibria in Organic Chemistry*. R. E. Krieger Publishing Company, Hunrington, NY (1981).

9. a) T. W. Bentley, G. Llewellyn. *Prog. Phys. Org. Chem.* 17, 121–158 (1990). b) T. W. Bentley. In *Nucleophilicity (Advances in Chemistry Series Vol. 215)* (J. M. Harris, S. P. McManus, eds.), pp. 255–268. American Chemical Society, Washington, D. C. (1987). c) K. Takeuchi, Y. Ohga, T. Ushino, M. Takasuka. *J. Org. Chem.* 62, 4904–4905 (1997).

10. a) C. D. Ritchie. *Acc. Chem. Res.* 5, 348–354 (1972). b) C. D. Ritchie. *Can. J. Chem.* 64, 2239–2250 (1986).

11. a) J. P. Richard, W. P. Jencks. *J. Am. Chem. Soc.* 104, 4689–4691 (1982). b) J. P. Richard, W. P. Jencks. *J. Am. Chem. Soc.* 104, 4691–4692 (1982). c) J. P. Richard, M. E. Rothenberg, W. P. Jencks. *J. Am. Chem. Soc.* 106, 1361–1372 (1984).

12. R. A. McClelland, V. M. Kanagasabapathy, N. S. Banait, S. Steenken. *J. Am. Chem. Soc.* 113, 1009–1014 (1991).

13. a) R. A. McClelland. *Tetrahedron* 52, 6823–6858 (1996). b) R. A. McClelland. In *Organic Reactivity: Physical and Biological Aspects* (B. T. Golding, R. J. Griffin, H. Maskill, eds.), pp. 301–319. The Royal Society of Chemistry, Cambridge (1995). c) P. K. Das. *Chem. Rev.* 93, 119–144 (1993).

14. L. A. P. Kane-Maguire, E. D. Honig, D. A. Sweigart. *Chem. Rev.* 84, 525–543 (1984).

15. a) L. A. P. Kane-Maguire, C. A. Mansfield. *J. Chem. Soc. Chem. Commun.* 540–541 (1973). b) L. A. P. Kane-Maguire, C. A. Mansfield. *J. Chem. Soc. Dalton Trans.* 2192–2196 (1976). c) G. R. John, C. A. Mansfield, L. A. P. Kane-Maguire. *J. Chem. Soc. Dalton Trans.* 574–578 (1977). d) G. R. John, L. A. P. Kane-Maguire. *J. Chem. Soc. Dalton Trans.* 1196–1199 (1979). e) T. I. Odiaka, L. A. P. Kane-Maguire. *Inorg. Chim. Acta* 37, 85–87 (1979). f) G. R. John, L. A. P. Kane-Maguire. *Inorg. Chim. Acta* 48, 179–183 (1981). g) G. R. John, L. A. P. Kane-Maguire, T. I. Odiaka, C. Eaborn. *J. Chem. Soc. Dalton Trans.* 1721–1727 (1983).

16. Reviews: a) H. Mayr. *Angew. Chem.* 102, 1415–1428 (1990); *Angew. Chem. Int. Ed. Engl.* 29, 1371–1384 (1990). b) H. Mayr, M. Patz. *Angew. Chem.* 106, 990–1010 (1994); *Angew. Chem. Int. Ed. Engl.* 33, 938–957 (1994). c) H. Mayr, O. Kuhn, M. F. Gotta, M. Patz. *J. Phys. Org. Chem.* in print. d) see also: Y. Wang, L. M. Dorfman. *Macromolecules* 13, 63–65 (1980).

17. H. Sakurai. *Pure Appl. Chem.* 54, 1–22 (1982).

18. a) H. Mayr. In *Selectivities in Lewis Acid Promoted Reactions* (D. Schinzer, ed.), Vol. 289, pp. 21–36. NATO ASI Series C (1989). b) H. Mayr, C. Schade, M. Rubow, R. Schneider. *Angew. Chem.* 99, 1059–1060 (1987); *Angew. Chem. Int. Ed. Engl.* 26, 1029–1030 (1987).

19. a) H. Mayr, R. Schneider, C. Schade, J. Bartl, R. Bederke. *J. Am. Chem. Soc.* 112, 4446–4454 (1990). b) H. Mayr, R. Schneider, B. Irrgang, C. Schade. *J. Am. Chem. Soc.* 112, 4454–4459 (1990). c) H. Mayr, R. Schneider, U. Grabis. *J. Am. Chem. Soc.* 112, 4460–4467 (1990).

20. H. Mayr, M. Roth, R. Faust. *Macromolecules* 29, 6110–6113 (1996).

21. H. Mayr, G. Gorath. *J. Am. Chem. Soc.* 117, 7862–7868 (1995).

22. O. Kuhn, D. Rau, H. Mayr. *J. Am. Chem. Soc.* 120, 900–907 (1998).

23. H. Mayr, D. Rau. *Chem. Ber.* 127, 2493–2498 (1994).

24. H. Mayr, J. Henninger, T. Siegmund. *Res. Chem. Intermed.* 22, 821–838 (1996).

25. a) M. Patz, H. Mayr. *Tetrahedron Lett.* 34, 3393–3396 (1993). b) J. Burfeindt, M. Patz, M. Müller, H. Mayr. *J. Am. Chem. Soc.* 120, 3629–3634 (1998).

26. M. Patz. PhD thesis, Technische Hochschule Darmstadt, 1994.

27. H. Mayr, K.-H. Müller, D. Rau. *Angew. Chem.* 105, 1732–1734 (1993); *Angew. Chem. Int. Ed. Engl.* 32, 1630–1632 (1993).

28. a) H. Mayr, M. Hartnagel, K. Grimm. *Liebigs Ann.* 55–69 (1997). b) H. Mayr, A. R. Ofial. *Tetrahedron Lett.* 38, 3503–3606 (1997). c) M.-A. Funke, H. Mayr. *Chem. Eur. J.* 3, 1214–1222 (1997).

29. a) A. Pross. *Acc. Chem. Res.* 18, 212–219 (1985). b) A. Pross, S. S. Shaik. *Acc. Chem. Res.* 16, 363–370 (1983).

30. a) B. A. Sim, P. H. Milne, D. D. M. Wayner. *J. Am. Chem. Soc.* 112, 6635-6638 (1990). b) D. D. M. Wayner, D. J. McPhee, D. Griller. *J. Am. Chem. Soc.* 110, 132-137 (1988). c) D. Griller, D. D. M. Wayner. *Pure Appl. Chem.* 61, 717-724 (1989). d) D. D. M. Wayner, B. A. Sim, J. J. Dannenberg. *J. Org. Chem.* 56, 4853-4858 (1991). e) S. Fukuzumi, S. Koumitsu, K. Hironaka, T. Tanaka. *J. Am. Chem. Soc.* 109, 305-316 (1987). f) S. Fukuzumi, T. Kitano. *Perkin Trans. 2* 41-45 (1991). g) H. Volz, W. Lotsch. *Tetrahedron Lett.* 2275-2278 (1969). h) K. Okamoto, K. Komatsu, O. Murai, O. Sakaguchi. *Tetrahedron Lett.* 4989-4992 (1972).

31. a) J. W. Bunting. *Heterocycles* 14, 2015–2045(1980). b) J. W. Bunting. *Bioorg. Chem.* 19, 456–491 (1991).

32. a) J. P. Richard, V. Jagannadham, T. L. Amyes, M. Mishima, Y. Tsuno. *J. Am. Chem. Soc.* 116, 6706–6712 (1994). b) T. L. Amyes, J. P. Richard, M. Novak. *J. Am. Chem. Soc.* 114, 8032–8041 (1992).

33. a) C. Schade, H. Mayr. *Tetrahedron* 44, 5761–5770 (1988); and references therein. b) J.-P. Dau-Schmidt. PhD thesis. Universität zu Lübeck (1992).

34. a) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. P. Stewart. *J. Am. Chem. Soc.* 107, 3902–3909 (1985). b) AM1 calculations were performed with the program MOPAC 6.01 by J. P. Stewart, University of Texas at Austin, Austin, TX.

35. H. Mayr, M. Hartnagel. *Liebigs Ann.* 2015–2018 (1996).

36. M. Patz, H. Mayr, J. Bartl, S. Steenken. *Angew. Chem.* 107, 519–521 (1995); *Angew. Chem. Int. Ed. Engl.* 34, 490–492 (1995).