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When Does Hammond's Postulate Predict Stabilities of Carbocations?

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Dedicated to Professor Helmut Schwarz, highly esteemed colleague and friend, on the occasion of his 80th birthday.

Abstract: Hammond's postulate, which relates the rate of formation of an unstable intermediate to the energy of this intermediate, has widely been used to determine stabilities of carbocations. However, the rates of formation of highly stabilized carbocations R^+ by ionization of R–X are only weakly or not at all correlated with their stabilities, because the corresponding activation energies are strongly affected by intrinsic barriers. In this article we will show that consideration of the rate of the reverse reaction allows one to define the range in which Hammond's postulate holds and when its predictive power fades as the role of intrinsic barriers is gaining importance. The ambiguity of the term "carbocation stability" is discussed. Kinetic data and quantum chemical calculations show that vinyl cations are not extraordinarily high energy intermediates, but that high intrinsic barriers account for their slow formation from vinyl halides and their rather slow reactions with nucleophiles.

Keywords: linear free energy relationships · solvolysis · kinetics · intrinsic barriers · vinyl cations

1. Introduction

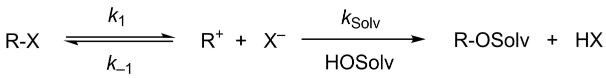
Hammond's postulate has become one of the most used tools in the discussion of reaction mechanisms.[1] While elucidating relationships between rates and equilibria of chemical reactions Hammond postulated: "*If two states, as for example, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small reorganization of the molecular structures.*"[2] With reference to Ingold's seminal textbook,[3] Hammond referred to S_N1 reactions as an example for the applicability of the postulate "*In a similar manner it is observed that the rates of production of carbonium ions from alkyl halides and similar substances generally may be correlated with the expected variations in the free energies of the ionization reactions.*"[2]

In this review we will discuss the range of validity of this correlation. In other words, but less precisely:[4] "When do the rates of formation of carbocations[5] from alkyl halides and related substrates give information about the stabilities of carbocations?"

2. Characterizing Transition States of Alkyl Halide Heterolyses

2.1 Application of the Principle of Microscopic Reversibility

For common solvolysis reactions, as described in Figure 1, the carbocation character of the transition states can be derived from the principle of microscopic reversibility.[6]



$$\text{R-X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R}^+ + \text{X}^- \xrightarrow[\text{HOSolv}]{k_{\text{Solv}}} \text{R-OSolv} + \text{HX}$$

Figure 1. Simplied solvolysis scheme for S_N1 reactions.

As illustrated in Figure 2, the activation Gibbs energies ($\Delta G^{\ddagger}$) for the formation of carbenium ions R^+ equal the corresponding Gibbs energies of ionization (ΔG_r°) if the recombinations of R^+ with X^- proceed without a barrier, i.e., if the reverse reaction is diffusion-controlled (Figure 2a). If the combination of R^+ with X^- involves a barrier, $\Delta G^{\ddagger}$ will be greater than ΔG_r° for the formation of the carbenium intermediate (Figure 2b). In order to differentiate between these two cases, we must know the rate constants for the reactions of R^+ with X^-, that is, k_{-1} in Figure 1.

Different methods have been used to determine rate constants for the reactions of various types of carbocations, in particular tritylium ions,[7] aryl substituted allyl cations,[8] and benzhydrylium ions (aryl_2CH^+)[9a,b] with halide ions and related nucleophiles. Let us now focus on the reactions of

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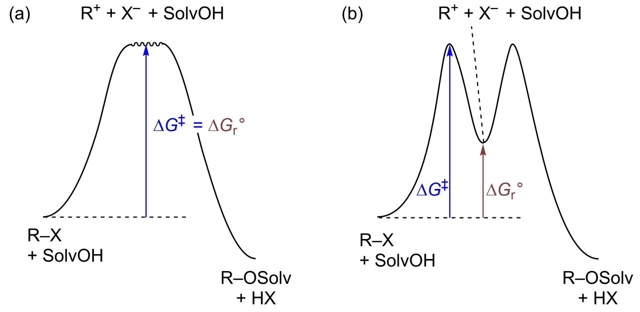

Figure 2. Gibbs energy profiles for S_N1 reactions with different rates of ion recombination.

benzhydrylium ions, which have most intensively been investigated.[10]

2.2 Transition States of the Reactions of Benzhydrylium Ions with Chloride and Bromide Ions

For measuring the rates of reaction of halide ions (Hal^-) with benzhydrylium ions, solutions of benzhydryl 4-cyanophenolates in aqueous or alcoholic solutions of tetrabutylammonium halides were irradiated with a 7 ns laser pulse ($\lambda = 266$ nm) to give benzhydrylium ions,[11] which reacted either with halide ions Hal^- or with the solvent to give stable products (Figure 3a). The observed rate constant for the decay of the benzhydrylium ion concentration (k_{obs}) under the conditions of the laser flash experiments is described by equation (1).[9a]

$$k_{obs} = k_{-1}[Hal^-] + k_{Solv} \qquad (1)$$

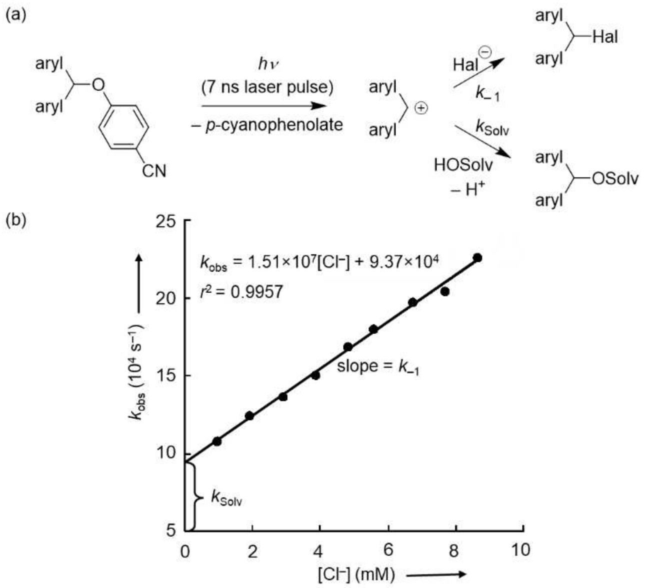

Figure 3. (a) Reactions of laser-flash photolytically generated benzhydrylium ions in aqueous or alcoholic solutions of tetrabutylammonium halides. (b) Linear correlation of pseudo-first-order rate constants (20 °C) of the reactions of the bis(*p*-anisyl)methylium ion with Cl^- in 50% aq acetonitrile with the concentration of $Bu_4N^+Cl^-$ (with data from ref [9a]).

As shown in Figure 3b, the first-order rate constants k_{obs} derived from the mono-exponential decays of the benzhydrylium absorbances increased with increasing concentration of the halide ions, and the intercepts of these correlations corresponded to the rate constants of the reactions of the benzhydrylium ions with the solvent (k_{Solv}).[9a] Recombination with phenolate ions is negligible because of their low concentration. The rate constants (k_{Solv}) determined in this way agreed with those determined by analogous experiments in the absence of halide additives.[9c]

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Figure 4 plots the rate constants (lg k) for the reactions of benzhydrylium ions with halide ions and the solvent against the empirical electrophilicity parameters E defined by equation (2).[10,12]

$$\lg k(20\,^\circ\mathrm{C}) = s_\mathrm{N}(E + N) \tag{2}$$

One can see that alkoxy-substituted benzhydrylium ions react with Cl^- and Br^- in 50 % aqueous acetonitrile (50W50AN) with rate constants below the diffusion limit, i. e., over small barriers. As a consequence, the activation Gibbs energies ($\Delta G^{\ddagger}$) for the solvolyses of alkoxy-substituted benzhydryl chlorides and bromides are slightly greater than the corresponding ionization Gibbs energies ($\Delta G_\mathrm{r}^\circ$). Extrapolation of these curves to the right indicates that reactions of these halide ions with carbocations of $E \geq 5$, including the unsubstituted benzhydrylium ion ($E = 5.47$),[13] will be diffusion-controlled. Given that Hammond's postulate is applicable in the diffusion-controlled range of the reverse reactions, one can generalize that the rates for the generation of carbocations of electrophilicity $E \geq 5$ from R–Cl or R–Br in 50 % aqueous acetonitrile provide accurate values for ionization energies.[14]

Even though the activation Gibbs energies for the ionizations of alkoxy-substituted benzhydryl chlorides in aqueous solution do not exactly reproduce the ionization Gibbs energies, the barriers for the reactions of the corresponding benzhydrylium ions with Cl^- are so low that the corresponding carbenium ions can still be considered as suitable, though not perfect models for the transition states of the ionization of the benzhydryl chlorides, i. e., Hammond's postulate still applies. Within a series of related reactions, ionization rates can be used to derive relative stabilities of carbocations.

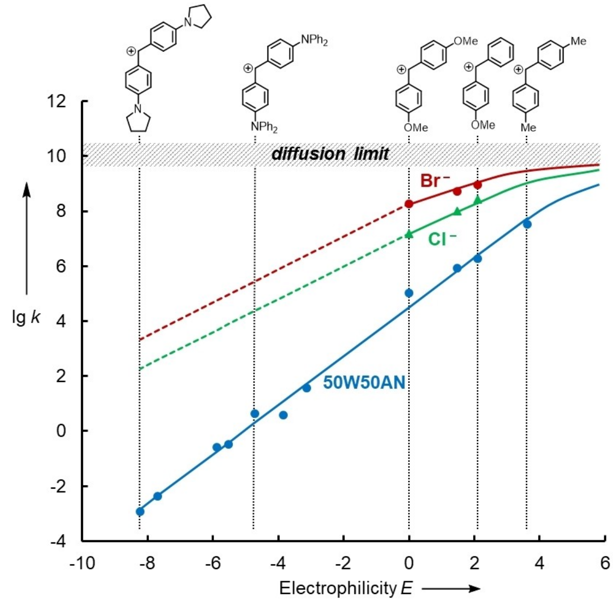

Figure 4. Second-order rate constants (lg k_{-1}) for the reactions of benzhydrylium ions with chloride and bromide ions in 50 % aqueous acetonitrile (50W50AN) and first-order rate constants k_Solv of the corresponding reactions with the solvent 50W50AN against the empirical electrophilicity parameters E of the benzhydrylium ions (with k_{-1} and k_Solv at 20 °C from ref [9a,c]).

Extrapolation of the correlation lines in Figure 4 to the left shows that increasing stabilization of the carbenium ions further reduces the rate constants of the reactions. For the reaction of chloride ions with the bis(4-dimethylamino)-substituted benzhydrylium ion ($E = -7.02$)[13] in 50W50AN one can derive a second-order rate constant of approximately $k_2 = 1000\ \mathrm{M^{-1}\,s^{-1}}$ at 20 °C using the N and s_N parameters for Cl^- in 50W50AN from ref. [9a,13] This rate constant is seven orders of magnitude below the diffusion limit with the consequence that Hammond's postulate should not be applicable for deriving the stabilities of the amino-substituted benzhydrylium ions from the rates of the corresponding ionization processes. This is only a hypothetical consideration, however, because the reverse reactions are so fast that amino-substituted benzhydryl chlorides and bromides are ionic and do not exist as covalent compounds in polar solvents.

In order to investigate ionization processes yielding highly stabilized carbocations, such as amino-substituted benzhydrylium ions, it is necessary to use substrates R–X with leaving groups X^- (nucleofuges) which are more Lewis-basic than halide ions.

3. Ionization Rates of Amino-Substituted Benzhydryl Carboxylates

Carboxylate ions fulfill this criterion, and as illustrated in Figure 5, covalent amino-substituted benzhydryl carboxylates were formed by treating solutions of benzhydryl tetrafluoroborates in acetonitrile or acetone with tetrabutylammonium carboxylates. Mixing the solutions of the covalent benzhydryl carboxylates with aqueous acetonitrile or acetone led to regeneration of the blue benzhydrylium ions, the rate of which could be monitored photometrically.[9b] In some cases, it was also possible to measure rates of ion combination in acetonitrile or acetone containing 10 or 20 % water which allowed us to construct complete energy profiles for ionization of covalent benzhydryl carboxylates and the corresponding ion combination in the same solvent (Figure 6b).[9b]

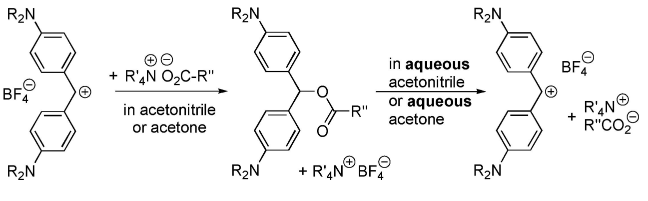

Figure 5. Formation and heterolysis of covalent benzhydryl carboxylates.

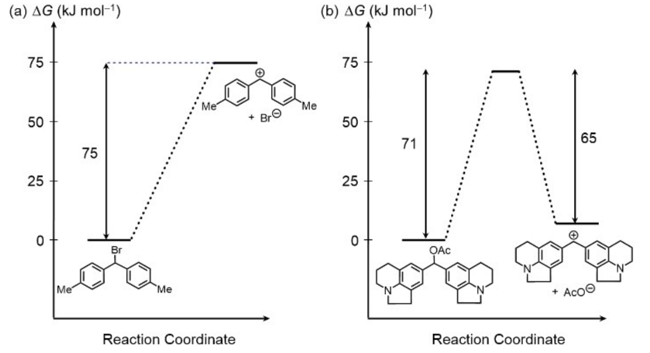

Figure 6. Simplified free energy profiles (25 °C) for ionizations of benzhydryl derivatives in 80 % aqueous acetone (encounter complexes not specified): (a) for an alkyl-substituted benzhydryl bromide and (b) an amino-substituted benzhydryl acetate (with data from ref [9b]).

Figure 6 illustrates the fundamental difference between the ionizations of benzhydryl halides and benzhydryl acetates. Though both ionizations proceed with similar activation Gibbs energies in 80 % aqueous acetone, Hammond's postulate (transition state of the ionization reactions resembling the carbocations) holds only for ionizations of alkyl chlorides and bromides (Figure 6a), but not for alkyl acetates and benzoates (Figure 6b), because only in the first case the rates of ion recombination are diffusion-controlled or close to diffusion control.[9a,b]

Can S_N1 reactions of benzhydryl acetates also proceed with diffusion-controlled ion recombinations? In principle yes! Using equation (2), one can calculate that the reactions of acetate ions ($N \approx 12.5$, $s_N \approx 0.6$)[9b,13] with benzhydrylium ions of electrophilicity $E \geq 4$ will be diffusion controlled in 80 % aqueous acetone. From the correlations given in ref.[15] one can derive, however, that ionizations of covalent benzhydryl acetates in 80 % aqueous acetone to give carbocations of $E \geq 4$ would require reaction times of more than 10^2 years at 25 °C.[16] Thus, in practice heterolytic C–O cleavages of alkyl acetates will only be encountered with substrates which yield highly stabilized carbocations; as discussed above, for such reactions Hammond's postulate is not applicable. From their nucleofugality parameters[15] one can derive that trifluoroacetates and carbonates are borderline cases.

The conclusion that ionizations of benzhydryl acetates in aqueous acetone do not proceed via carbocation-like transition states is also confirmed by the solvent-dependence of the corresponding solvolysis rates (Figure 7). Winstein and Grunwald reported that solvolysis rate constants follow equation (3), where k and k_0 are rate constants for solvolysis of R–X in a given solvent and in 80 % aqueous ethanol, respectively.[17a,b] Since the solvolysis of *tert*-butyl chloride was defined as the reference reaction ($m = 1.0$), the solvent ionizing power Y expresses the reactivity of *tert*-butyl chloride in a certain solvent relative to 80 % aqueous ethanol ($Y = 0$), and m expresses the sensitivity of the solvolysis rate constant of a certain substrate to variation of the solvent ionizing power Y.[17a,b]

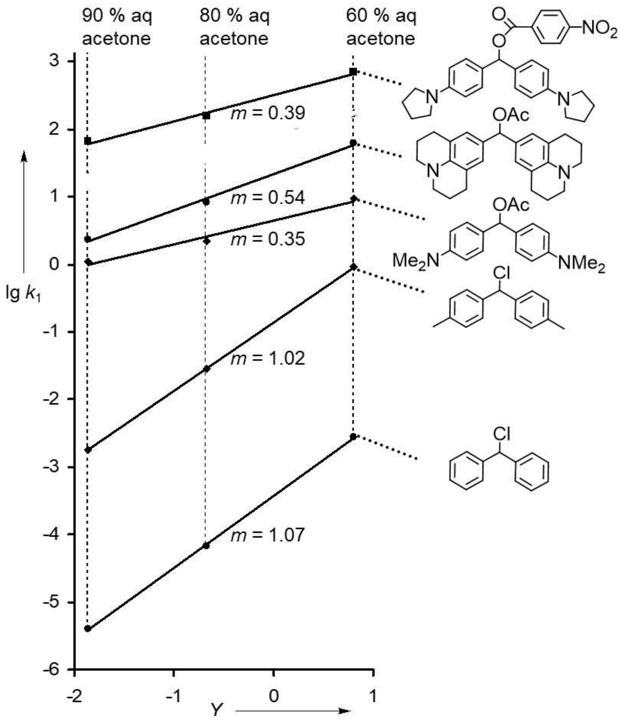

Figure 7. Correlation of rate constants (lg k_1) for ionization of some benzhydryl derivatives (at 25 °C) with solvent ionizing power Y (with data from ref [9b]).

$$\lg\,(k/k_0) = mY \tag{3}$$

Numerous S_N1 reactions have been found to have sensitivities $m \approx 1$, while m values < 0.5 were observed for S_N2 reactions.[17] Accordingly, Figure 7 shows the susceptibilities $m = 1.07$ and 1.02 for the solvolysis rates of the benzhydryl chlorides which ionize via carbocation-like transition states. The susceptibilities of the ionization rates of the benzhydrylium carboxylates ($0.35 \leq m \leq 0.54$) are comparable to m values of S_N2 reactions, in line with not fully developed carbocation character in the corresponding transition states.[9b]

Rate constants of the reactions of tritylium ions with acetate and benzoate ions in aqueous acetonitrile can also be calculated to be far below the diffusion limit,[7c] with the consequence that ionizations of the corresponding covalent trityl (Tr) acetates $Ar_3C{-}OAc$ do not have carbocation-like transition states.[18] Winstein-Grunwald plots[17] of lg k vs Y confirm this conclusion. Figure 8 illustrates that the susceptibility decreases with increasing stability (that is, decreasing Lewis acidity) of the corresponding carbocations from $m = 0.58$ for $Ph_3C{-}O_2CCH_3$ to $m = 0.21$ for the bis-(4-dimethylamino)-substituted trityl acetate.

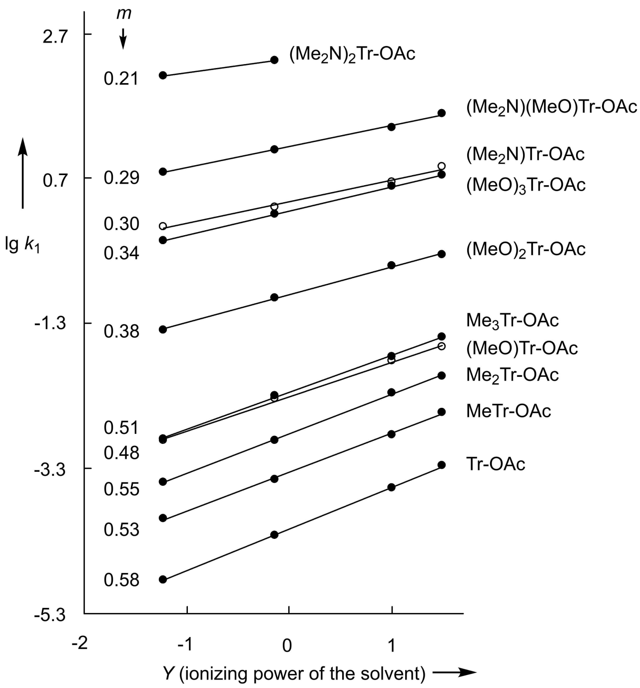

Figure 8. Plot of lg k_1 of trityl acetates (at 25 °C) vs. Y of aqueous acetonitrile solutions (Tr is used as an abbreviation for the triphenylmethyl (trityl) moiety. Substituents are attached to 4-positions of the phenyl groups. For example, Tr-OAc represents the parent trityl acetate and Me$_3$Tr-OAc refers to the 4,4',4''-trimethyl-substituted trityl acetate. $Y = -1.23$ (90AN10W), -0.14 (80AN20W), 1.00 (60AN40W), and 1.50 (50AN50W), with data from ref [18]).

4. Correlations between Ionization Rate Constants and Thermodynamically Determined Carbocation Stabilities

So far, we have discussed whether "carbocation stabilities" can be derived from kinetic data. "Stability" is a thermodynamic quantity, however,[19] and we will now consider how the rates of ionizations of R–X are correlated with thermodynamics. Let us first keep in mind that only in the case of isomeric carbocations, relative stabilities can unambiguously be derived from the difference of their Gibbs energies in a certain environment. Reference reactions, which may relate to the Lewis or Brønsted acidities of carbocations, must be defined for comparing the stabilities of non-isomeric carbocations, as explicitly discussed by Hine[20] and later specified by us.[21] In the context of this article, we will focus on Lewis acidities, since the reverse of the ionization of R–X corresponds to the combination of the Lewis acid R^+ with the Lewis base X^-. The problem of quantifying the stabilities of non-isomeric carbocations is illustrated in Figure 9, which compares the Lewis acidities of the isopropyl and *tert*-butyl cation with respect to hydride, chloride, and hydroxide as reference Lewis bases.

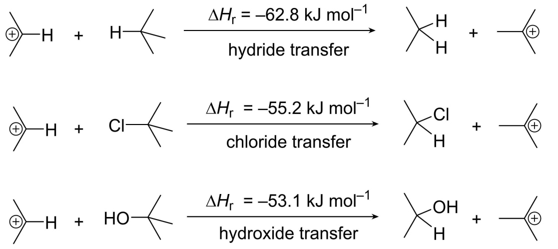

Figure 9. Comparison of the "stabilities" of isopropyl and *tert*-butyl cations. See ref. [21a,b] for origin of these numbers.

All three group transfer reactions are highly exothermic, showing that the extra methyl group affects the carbocations more than their neutral precursors. Using laboratory slang, we may state that the *tert*-butyl cation is 53 to 63 kJ mol^{-1} more stable than the isopropyl cation, but the precise value depends on the arbitrary choice of the reference base.

The best-known Lewis acidity scales for carbocations are the pK_{R+} scales,[22] which describe the affinities of carbocations toward the hydroxide ion, usually in aqueous solution. Arnett derived stability scales of carbocations from the heats of ionization of alcohols and alkyl chlorides under superacidic conditions.[23a] From the slope of 0.89 of the correlation of the activation Gibbs energies of S$_N$1 reactions of alkyl chlorides in ethanol with the corresponding heats of ionization, Arnett, Petro, and Schleyer concluded that the carbocation character is "*very largely*" developed in the solvolysis transition states, i. e., Hammond's postulate is applicable.[23b]

Wide-ranging Lewis acidity scales of benzhydrylium ions in dichloromethane and acetonitrile have been based on Lewis adduct formation from benzhydrylium ions and various Lewis bases (Figure 10).[21c,24]

Studies of the equilibrium constants K of the reactions of *p*- and *m*-substituted benzhydrylium ions with pyridines, phosphines, *tert*-amines, dialkyl sulfides, and related Lewis bases showed that the relative Lewis acidities (*LA*) of the benzhydrylium ions were almost independent of the nature of the Lewis base, which we explained by the similar surroundings at the reactive center of the benzhydrylium ions. By using strong and weak Lewis bases as references it was possible to measure equilibrium constants for reactions with benzhydrylium ions of widely differing Lewis acidity, and by using the method of overlapping correlation lines we arrived at a Lewis acidity scale covering 17.6 units of lg K as reflected by the

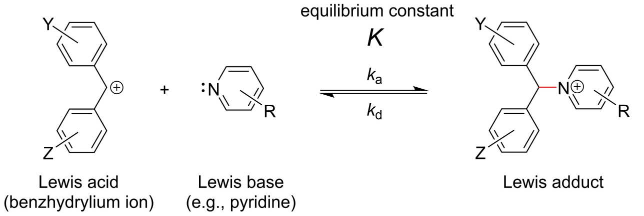

Figure 10. Determination of relative carbocation stabilities (Lewis acidities) from equilibrium constants K.[24]

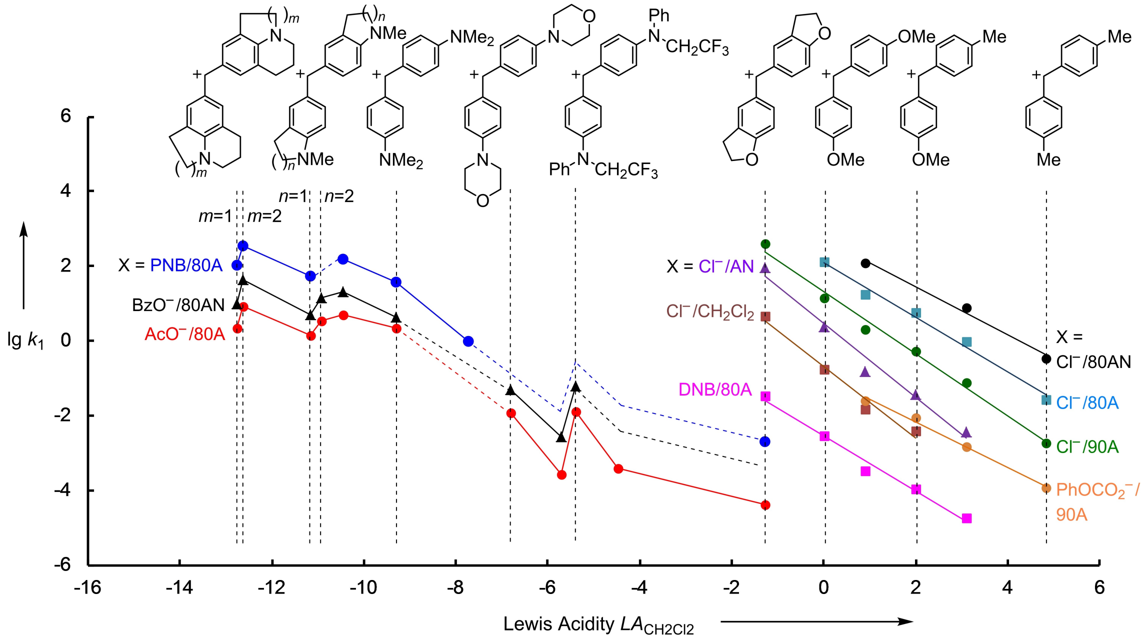

Figure 11. Correlation of heterolysis rate constants lg k_1(25 °C) for aryl$_2$CH–X with the Lewis acidities *LA* of benzhydrylium ions aryl$_2$CH$^+$ in dichloromethane (PNB = *p*-nitrobenzoate, DNB = 3,5-dinitrobenzoate, 80 A = 80/20 acetone/water; 90 A = 90/10 acetone/water; 80AN = 80/20 acetonitrile/water; data from ref [21c,24]).

abscissa of Figure 11. The linear correlation of this equilibrium-based "stability scale" for carbocations with DFT calculated methyl anion affinities confirmed its internal consistency.[21c,24]

When we now plot ionization rate constants (lg k_1) of benzhydryl chlorides and carboxylates against the Lewis acidities of the carbocations, LA_{CH2Cl2}, we arrive at the same conclusion as obtained by considering the rates of forward and backward reactions: While the ionization rate constants of benzhydryl chlorides correlate linearly with the carbocation stabilities based on equilibrium constants (that is, Lewis acidities of carbocations), the ionization rates of benzhydryl carboxylates, which yield the highly stabilized amino-substituted benzhydrylium ions, correlate poorly with the corresponding Lewis acidities of the carbocations.

One can even see cases, where the more stable carbocation R_A^+ is formed more slowly than the less stable carbocation R_B^+, as schematically illustrated in Figure 12. Obviously, the differences of the intrinsic barriers override the differences in Lewis acidities of the carbocations. When the differences in Lewis acidities are small, one can even come to the counterintuitive situation, that carbocations which are formed more slowly, also react more slowly with nucleophiles.[9b,21c,24]

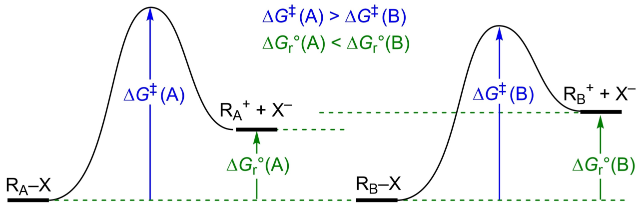

Figure 12. Effect of different intrinsic barriers on energy profiles for the generation of stable carbocations.

The examples discussed in the preceding chapters show that it is the rate of the reverse reaction (ion recombination) and not the rate of ionization which allows one to decide whether the transition state of an ionization process is carbocation-like or not, i. e., whether Hammond's postulate is applicable or not.

With his postulate Hammond referred to "*unstable intermediates*". But what are unstable intermediates? The *tert*-butyl cation is an unstable intermediate in aqueous or alcoholic solution, where it rapidly reacts with the solvent, but not in superacidic solution where it survives for days because it does not find a sufficiently strong Lewis- or Brønsted basic reaction partner. By considering the rate constants for the reactions of R^+ with the leaving group X^- as a criterion, we arrived at the conclusion that most benzhydrylium ions generated from R–Cl and R–Br under typical solvolytic conditions are unstable intermediates in water or alcohols and are formed via carbocation-like transition states. Since heterolytic cleavages of the R–O bonds of R–OAc usually only take place with substrates that yield highly stabilized carbocations, such as the amino-substituted benzhydrylium ions, which are not "reactive intermediates", the non-applicability of Hammond's postulate is in line with our intuition. Intuition has been misleading, however, when interpreting solvolysis rates of vinyl halides and tosylates.

5. Vinyl Cations

For many years the very slow solvolysis rates of vinyl halides and tosylates have been assigned to the low stabilities of vinyl cations.[25] It was rationalized by the fact that in vinyl cations the formal positive charge is located on an sp-carbon and not on an sp^2-carbon as in tricoordinated carbenium ions. However, this explanation conflicted with the observation of common ion rate depression in solvolysis reactions of vinyl halides and tosylates.[25]

Common ion rate depression, i. e., reduction of the rate of solvolysis of R–X in the presence of a salt M^+ X^-, is rationalized by the reaction of the initially formed carbocation R^+ with the common ion X^- leading to regeneration of the covalent R–X (Figure 1).[3,26] If the ion R^+ is highly electrophilic, it reacts rapidly with excess solvent, resulting in a first-order reaction with the rate constant k_1. On the other hand, if the carbocation R^+ is sufficiently long-lived, the more nucleophilic anion X^- may compete with the less nucleophilic solvent which is present in high concentration and thus lead to a reduction of the overall solvolysis rate.[3,26]

In view of these relationships, the widespread appearance of common ion rate depression in the solvolysis of many α-arylvinyl systems[27a] was considered most surprising, since according to Hammond's postulate the observed low ionization rates were expected to indicate the formation of highly unstable cations of low selectivity.[27b] However, already in 1979 a comprehensive review on common ion-return in vinyl solvolyses stated "*If the selectivity is directly related to the lifetime and the stability of the ions….., then the α-arylvinyl cations….are long-lived and remarkably stable*".[27c]

This conclusion has later been confirmed. McClelland and Steenken reported that the laser-flash photolytically generated 1-(*p*-anisyl)-2,2-diphenyl-vinyl cation reacts 200-times more slowly with the solvent trifluoroethanol[28] than the parent benzhydrylium ion,[29] though the solvolysis of the precursor vinyl bromide in 80 % aqueous ethanol[30] was known to be 1.6 million times slower than that of benzhydryl bromide[31] under the same conditions (Figure 13). If Hammond's postulate were applicable, the much slower ionization of the vinyl bromide would imply a much lower stability and higher reactivity of the resulting vinyl cation compared to the parent benzhydrylium ion, i. e., contrary to the observed reaction rates. Systematic investigations of the kinetics of the reactions of the 1-(*p*-anisyl)-2,2-diphenyl-vinyl cation with a large variety of nucleophiles confirmed that its electrophilic reactivity is much below that of the parent benzhydrylium ion.[32]

Let us now compare the Gibbs energy profiles for the solvolyses of benzhydryl bromide and 1-bromo-1-(*p*-anisyl)-2,2-diphenylethene (Figure 14). The solvolysis rate of benzhydryl bromide has directly been measured,[31] and laser-flash photolytically generated benzhydrylium ions underwent diffusion-controlled reactions with bromide ions in all solvents investigated.[9a] As discussed at the beginning of this article, application of the principle of microscopic reversibility implies that the ionization Gibbs energy of benzhydryl bromide equals the activation Gibbs energy, which is calculated by the Eyring equation from the measured solvolysis rate constant.

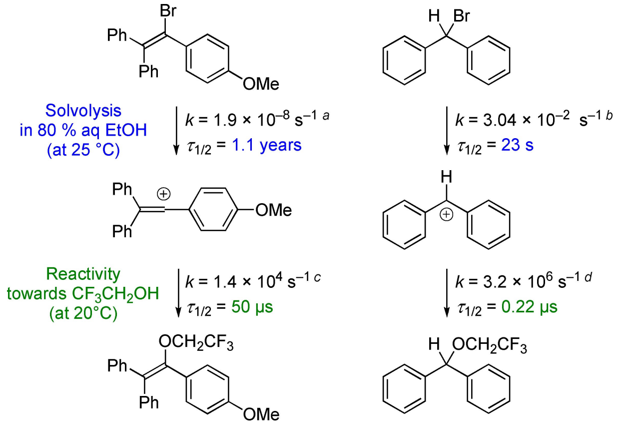

Figure 13. Comparison of the rates of generation of vinyl and benzhydryl cations in 80% aqueous ethanol and the rates of their reactions with trifluoroethanol. a) Calculated from activation parameters in ref. [30]; b) ref. [31]; c) ref. [28]; d) ref [29].

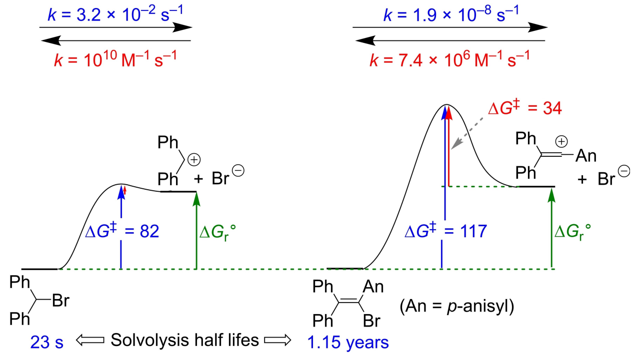

Figure 14. Gibbs energy profiles for the solvolyses of bromodiphenylmethane and 1-bromo-1-(*p*-anisyl)-2,2-diphenylethene in 80% aqueous ethanol (25 °C, Gibbs energies in kJ mol^{-1}).

In contrast to the diffusion-controlled reactions of bromide ions with benzhydrylium ions, a rate constant 3.7×10^6 M^{-1} s^{-1} has been measured for the reaction of Br^- with the laser-flash photolytically generated 1-(*p*-anisyl)-2,2-diphenyl-vinyl cation in trifluoroethanol.[32] A slightly larger value (7.4×10^6 M^{-1} s^{-1}) was derived for the corresponding reaction in 80 % aqueous ethanol from the correlations given in ref.[32] Combination of the barriers for forward and backward reaction gives an ionization Gibbs energy of 83 kJ mol^{-1} for the vinyl bromide in Figure 14, similar to that of benzhydryl bromide.

The comparable "stabilities" ($\Delta G_r°$) of the tricoordinated and dicoordinated carbenium ions derived from kinetic data in Figure 14 have been confirmed computationally. As shown by the quantum chemical calculations in Figure 15, the 1-(*p*-anisyl)-2,2-diphenylvinyl cation and the parent benzhydrylium ion have almost identical methyl anion and bromide ion affinities.[33] Thus, differences in intrinsic barriers have to

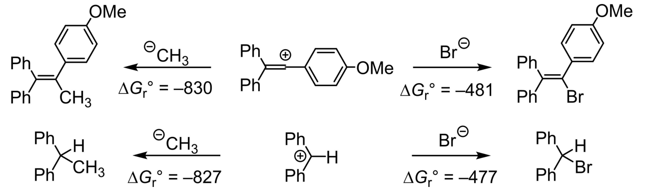

Figure 15. Calculated methyl anion affinities [B3LYP/6-311++G-(3df,pd)//B3LYP/6-31G(d,p)] and bromide anion affinities [TPSSTPSS/def2TZVP+GD3] in the gas phase (Gibbs energies in kJ mol^{-1}).

account for the smaller rates of formation and smaller rates of reactions of vinyl cations with nucleophiles compared to tricoordinated carbenium ions of comparable "stability".

Intrinsic barriers are related to reorganization energies and can be calculated, in rare cases also measured, from the rates of identity reactions.[34] Since one cannot define identity reactions for the ionization processes or ion recombinations of Figure 14, we had calculated the barriers for identity hydride shifts between tricoordinated and dicoordinated carbocations as illustrated for the hydride transfers between phenylethyl cations and phenylvinyl cations in Figure 16. The higher intrinsic barrier for the hydride transfer in Figure 16b indicates that sp^2/sp-rehybridizations require more reorganization energies than sp^3/sp^2-rehybridizations (Figure 16a), which explains the slower formations and slower reactions of vinyl cations compared to tricoordinated carbocations of comparable stability (more precisely: Lewis acidity).

In line with the moderate electrophilicities of vinyl cations, Niggemann has reported regio- and stereoselective reactions of vinyl cations, which makes them useful intermediates in organic synthesis.[35] The low electrophilicities of vinyl cations also enable their use in enantioselective C–H insertion reactions as recently demonstrated by Nelson and colleagues.[36]

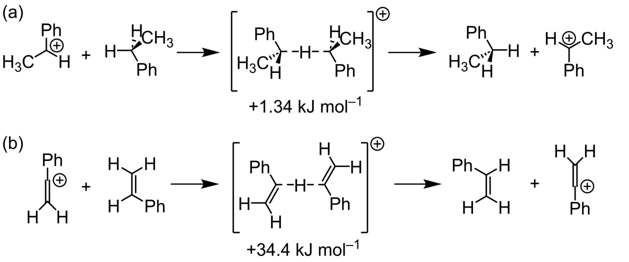

Figure 16. Activation Gibbs energies calculated (at the TPSSTPSS/def2TZVP+GD3//TPSSTPSS/def2TZVP+GD3 level of theory) for identity hydride transfer reactions between 1-phenylethyl and 1-phenylvinyl cations in the gas phase.

6. Epilogue

Our understanding of organic reactivity is founded on relationships between rates and thermodynamics of organic reactions. Bell-Evans-Polanyi relationships which show that in many reaction series rates increase with increasing exothermicity have coined our intuition.[37] Equation (4), which was developed by Leffler in 1953,[38] can be considered as the Gibbs energy equivalent of the Bell-Evans-Polanyi relationships.

$$\delta\Delta G^{\ddagger} = \alpha\delta\Delta G_r^{\circ} \qquad (4)$$

Assuming that the transition state is a blend of reactant and product configurations, Leffler interpreted α in eq. (4) as an indicator of the position of the transition state. With the assumption $0<\alpha<1$, he considered small values of α as evidence for early, reactant-like transition states, while α values close to 1 were believed to designate reactions with product-like transition states. Since Leffler's interpretation of α values close to 1 coincides with Hammond's postulate, both concepts are often merged by the term "Hammond-Leffler principle",[6] though Hammond (1955)[2] did not even refer to Leffler's 1953 analysis.

Whereas Leffler's interpretation of α (eq. 4) appears attractive, Bordwell's observation that deprotonations of nitroalkanes have α values around 1.5 clearly shows that α is not limited to the range $0<\alpha<1$, and therefore cannot be an indicator of the position of the transition state.[39] Using Shaik's configuration mixing model,[40] Pross and Shaik pointed out that normal rate-equilibrium relationships, i. e., validity of eq. (4), can only be expected for reaction series which may adequately be described by just two configurations, reactant and product, while reaction series which require at least one additional configuration may exhibit deviations. They emphasized that even for one-step processes the character of the transition state is not necessarily intermediate between that of reactants and products, because "*the transition state may take on characteristics which are only weakly present or even totally absent in both reactants and products*".[41] Pross pointed out that in identity reactions, e. g., isotope exchange reactions of the type $R–Cl + {}^*Cl^- \rightarrow R–{}^*Cl + Cl^-$, substituent variation affects $\Delta G^{\ddagger}$ while $\delta\Delta G_r^{\circ} = 0$ with the consequence that $\alpha = \delta\Delta G^{\ddagger}/0 = \text{infinity}$.[42] Nowadays many reaction series with α outside the range from 0 to 1 are known and it is indisputable that Leffler's α does not allow to localize the position of the transition state. But what about Hammond's postulate?

We have shown in this review that Hammond's postulate can be applied for deriving carbocation stabilities from ionization rates if the reverse reactions are diffusion controlled, but not if the reverse reactions are activation controlled. But how can one differentiate these cases? In Section 3 we have demonstrated that carbocations, which are isolable as persistent salts under normal chemical conditions, will most likely not be generated by ionization processes via carbocation-like transition states, i.e., Hammond's postulate is not applicable. The vinyl cation discussion shows, however, that also ionization processes that yield types of carbocations, which are commonly considered as "reactive intermediates", do not necessarily proceed via carbocation-like transition states. This situation is not restricted to vinyl cations, however, and extensive work by Richard and Amyes has shown that also generation and reactivities of CF_3-substituted carbenium ions are strongly affected by intrinsic barriers.[43]

Due to the availability of reliable quantum chemical calculations Hammond's postulate has lost its key role to derive carbocation stabilities from kinetic data. On the other hand, it is important to note that, because of the potential contributions of intrinsic barriers,[9b,15,44] care is needed when using Hammond's postulate for predicting ionization rates from quantum chemically derived carbocation stabilities.

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Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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