MOLECULAR BASIS OF LFER. SIMPLE MODEL FOR THE ESTIMATION OF BRØNSTED EXPONENT IN ACID-BASE CATALYSIS

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Dedicated to Professor Otto Exner on the occasion of his 80th birthday in recognition of his outstanding contributions to the area of physical organic chemistry.

A simple model was proposed allowing to estimate the Brønsted exponents in acid-base catalysis on the basis of the pK values of the species participating in the proton transfer process. The approach was tested using the experimental data on the basically catalyzed halogenation of carbonyl compounds and on the proton removal from nitroalkanes. It has been shown that the model is able to reproduce the Brønsted exponents not only in the case of "ordinary" Brønsted plots with the slope within the expected range 0–1 but also for unusual plots with negative slopes. In addition, the proposed model opens the possibility of calculation of the activation energies of a given proton transfer reaction and also provides straightforward theoretical justification for the validity of the Hammond postulate in these reactions.

Keywords: Acidity; Brønsted acids; Proton transfer; Brønsted equation; Analytic model.

One of the domains of organic reactivity which still resists to rigorous theoretical description to a considerable extent is the domain that deals with the relations between the structure and the reactivity. Because of inherent complexity of the underlying phenomena, various empirical rules and concepts still play an important role in the build-up of models allowing the rationalization of such relations. The first reported example of such relationships, often called the linear free energy relationships (LFER), is the Brønsted equation[1], which describes the relation between the catalytic rate constants k_B of an acid-base catalyzed reaction and the dissociation constants pK of the acids and/or bases used as the catalysts for this reaction. The most valuable quantity provided by this equation are the exponents (α and/or β), originally assumed to vary between 0 and 1, which are often used as an experimental probe for obtaining a detailed insight into the

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mechanism of proton transfer reactions. Because of importance of these mechanistic data, a lot of effort was devoted in the past years to the elaboration of theoretical models allowing to rationalize the existence of this originally empirical equation and, also, to justify the mechanistic interpretation of the parameters of this equation. In this respect, the most widely accepted approach is represented by the classical studies of Bell, Marcus and others[2–11], who proposed the models of proton transfer reactions based on the idea of intersecting potential energy (PE) hypersurfaces. Although these models have been able to rationalize many qualitative features of the Brønsted equation, such as the curvature of the Brønsted plots over wider regions of p*K*, none of them was realistic enough to allow the calculation of the actual numerical values of the Brønsted exponent in any particular case. Moreover, none of these models was able to rationalize the existence of unusual Brønsted plots with the slopes exceeding the originally assumed range between 0–1. Our aim in this study is just to address these problems and to propose a simple model in terms of which the numerical values of Brønsted exponents can be estimated not only for "normal" Brønsted plots with exponents within the expected range, but also in the case of unusual plots. In the following part the basic idea of the new proposed model will be presented.

THEORETICAL

The Brønsted equation is an empirical relationship that relates the catalytic rate constants k_B of a given reaction catalyzed by a series of acids or bases, to their dissociation constants.

$$\log k_B = \log G + \alpha \log K \qquad (1)$$

Since its discovery in 1924, this equation has been the subject of a wealth of studies aimed at the systematic investigation of the domains of its validity, as well as at the detailed understanding of the factors responsible for its existence[11–14]. In this respect, one of the important problems addressed by theoretical studies was the existence of deviations from the strict linearity suggested by the original equation (*1*), or the observation of Brønsted plots with unusual slopes exceeding traditional limits. Although the possibility of the curvature of the Brønsted plots was anticipated already in the original study by Brønsted[1], and subsequently corroborated by experimental studies by Eigen[13], a theoretical microscopic explanation for the existence of this curvature was offered by the Marcus theory[4,5] and more recently also by Lewis and More O'Ferrall[15] and Tupitsin[16]. Marcus theory is based on the model of intersecting parabolas, which are assumed to approximate the PE curves for the proton transfer process (*2*).

$$\mathrm{AH} + \mathrm{B} \rightleftharpoons \mathrm{BH}^+ + \mathrm{A}^- \qquad (2)$$

According to this model, the Gibbs energy of activation, $\Delta G^{\neq}$, is related, as a kinetic parameter, to the thermodynamic parameter, namely the standard Gibbs energy of reaction ΔG^0, through the so-called "intrinsic barrier", $\Delta G_0^{\neq}$, which is the Gibbs energy of activation, for the hypothetic process for which ΔG^0 is zero.

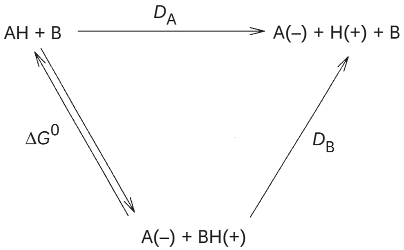
$$\Delta G^{\neq} = \Delta G_0^{\neq}(1 + \Delta G^0/4\Delta G_0^{\neq})^2 \qquad (3)$$

Within this approach, the Brønsted exponent is given by Eq. (*4*).

$$\alpha = \frac{\mathrm{d}\Delta G^{\neq}}{\mathrm{d}\Delta G^0} = \frac{1}{2}\left(1 + \frac{\Delta G^0}{4\Delta G_0^{\neq}}\right) \qquad (4)$$

Although this equation made it indeed possible to rationalize many qualitative aspects of the Brønsted relation, the model itself is still not realistic enough for quantitative purposes. This is due to the crudeness of approximations adopted in the derivation of basic equations (*3*) and (*4*). The most important of these approximations is the assumption that the PE curves governing the proton transfer process (*2*) can be represented by the intersecting parabolas, which, moreover, share the same harmonic oscillator force constants. In order to make the above simple model more realistic, the improvements were subsequently proposed that allowed to overcome both the above simplifying assumptions[7,8]. Thus, for example, in the study by Koeppl and Kresge[7], the original Marcus model was extended by allowing different harmonic potential force constants for the intersecting parabolae. In addition, another improvement was proposed by Bell[8], in which the original harmonic approximation of PE curves was replaced by a more realistic model of intersecting Morse curves. Although both these improvements certainly contributed to putting the original Marcus model on safer theoretical basis, none of the above models is still suited to practical calculation of actual Brønsted exponents. This is due to the fact that each of these models also relies on certain external parameters whose values are not accessible from experiment and whose knowledge requires the detailed microscopic information about the proton transfer. This is in particular the case of the parameter *a* which characterizes the distance separating the minima of both intersecting PE curves. Without the knowledge of this parameter, both the above models can only serve for a qualitative discussion of general trends rather than for actual quantitative calculations. In order to overcome this limitation we are going to propose a simplification of previous models[7,8], in terms of which the knowledge of the actual values of the parameter *a* can completely be avoided and which, at the same time, allows the calculation of actual numerical values of the Brønsted exponent in any particular case.

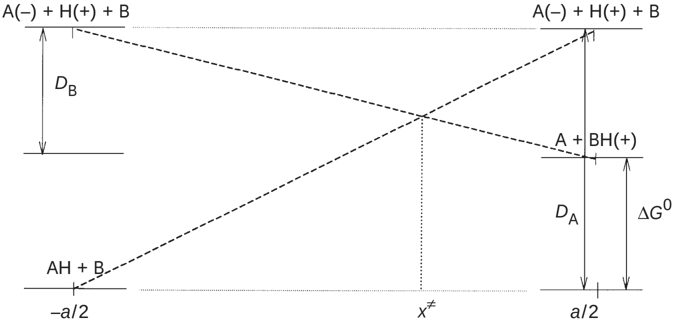
The basic idea of this simplification arises from the combination of previous models of intersecting PE curves[7,8] with the thermodynamic cycle (Scheme 1), governing the energetic relations in simple proton transfer reaction (*2*). The most important feature of the thermodynamic cycle is that it ascertains that the quantity ΔG^0, which in previous models was considered as an independent parameter, is in fact related to parameters D_A and D_B, which characterize the ease of the proton dissociation in acids AH and BH^+ (Eq. (*5*)).



SCHEME 1

$$\Delta G^0 = D_A - D_B \tag{5}$$

Both these parameters are thus closely related to the dissociation constants of acids AH and BH^+ and as such could also be, at least in principle, calculated by theoretical quantum chemical methods. As, however, such a completely theoretical approach still suffers from possible imperfections of the existing methods for the inclusion of the solvent effect, we prefer to base the practical applications of the new model on the semiempirical approach in which the quantities D_A and D_B are parametrized via the experimental p*K* values. However, the existence of the thermodynamic cycle governing the energetics of the proton transfer (*2*) is important for yet another reason. It reveals, namely, the main drawback of the original Marcus model[3,4] as well as its subsequent improvements[7,8]. Thus, for example, in the case of the models[3,4,7], the absence of the dissociation limits on the intersecting parabolic PE curves prevents these models from reflecting correctly the energetic restrictions in the proton transfer (*1*) imposed by the above thermodynamic cycle. This drawback could be, in principle, remedied using a more realistic approach[8] based on the idea of intersecting Morse curves, but the existence of the boundary condition (*5*), which relates the values of parameters D_A, D_B and ΔG^0, was not considered in the study[8] either. In view of the above drawbacks and in order to overcome the dependence of all the previous models on the knowledge of the microscopic parameter a, we propose a simplified approach in which the branches of intersecting parabolae and/or Morse curves are replaced by simple lines. The basic idea of such an approximation is depicted in Scheme 2. The advantage of this approximation is that although the parameter a still formally enters into the model, the dependence of the final formula for Brønsted exponent on this parameter is completely eliminated. This is straightforwardly evident from the final formulas for the Gibbs energy of the activation $\overrightarrow{\Delta G}^{\neq}$ for the forward reaction (Eq. (*6*)).



SCHEME 2

$$\overrightarrow{\Delta G}^{\neq} = \frac{D_A D_B}{D_A + D_B} + \frac{D_A \Delta G^0}{D_A + D_B} = \frac{D_A^2}{D_A + D_B} \qquad (6)$$

This equation implies that the only quantities determining the value of the Brønsted exponent are the parameters D_A and D_B , which are related to experimental pK of the substrate and the catalyst involved in the proton transfer.

$$\alpha = \frac{d\overrightarrow{\Delta G}^{\neq}}{d\Delta G^0} = -\frac{d\overrightarrow{\Delta G}^{\neq}}{dD_B} = \frac{D_A^2}{(D_A + D_B)^2} \qquad (7)$$

Similarly it is possible to show that the Brønsted exponent for the backward reaction, characterized by the activation Gibbs energy (*8*)

$$\overleftarrow{\Delta G^{\neq}} = \overrightarrow{\Delta G^{\neq}} - \Delta G^{0} = \frac{D_{\mathrm{B}}^{2}}{D_{\mathrm{A}} + D_{\mathrm{B}}} \tag{8}$$

is given by Eq. (*9*)

$$\beta = \frac{\mathrm{d}\overleftarrow{\Delta G^{\neq}}}{\mathrm{d}\Delta G^{0}} = -\frac{\mathrm{d}\overleftarrow{\Delta G^{\neq}}}{\mathrm{d}D_{\mathrm{B}}} = \frac{D_{\mathrm{B}}^{2} + 2D_{\mathrm{A}}D_{\mathrm{B}}}{(D_{\mathrm{A}} + D_{\mathrm{B}})^{2}}\ . \tag{9}$$

It is interesting to remark that the values of the exponents satisfy, as expected, the equation (*10*).

$$\alpha + \beta = 1 \tag{10}$$

After having derived the final master formulas, let us demonstrate, in the following part, practical applications of the proposed approach to the calculation of absolute values of Brønsted exponents for several systems, for which the experimental data are available in the literature.

RESULTS AND DISCUSSION

In order to demonstrate practical applicability of the proposed approach, let us start first with the comparison of calculated and experimental values of the Brønsted exponents for a selected set of acid-base catalyzed reactions with “normal” exponents within the traditional range 0–1. The most exhaustive study of the variation of the Brønsted exponent with the structure of the reacting substrate is provided by the studies of Bell and coworkers[11,17–19] who systematically investigated the acid-base catalyzed halogenation of carbonyl compounds. The experimental values of Brønsted exponents determined by Bell are summarized in Table I. The studied molecules include the broad class of carbonyl compounds ranging from acetone to acetylacetone; the same table also summarizes the values of the pK of the studied compounds. (There are some discrepancies between the values of pK and log R in the study[11] and in the original studies[17–19].) The values of pK were taken from the book by March[20] and from the paper by Guthrie[21]. The experimental values of α, summarized in the original studies[17–19], were determined from the Brønsted plots for a set of catalyst bases involving the anions of four aliphatic carboxylic acids, namely, acetic acid, glycolic acid, chloroacetic acid and pivalic acid. The theoretical values of Brønsted exponents were calculated according to formula (*8*) as a mean of four values corresponding to the above individual acids. For the purpose of maximum compatibility with the experimental studies by Bell, the D_B values were calculated from the dissociation constants pK of the acids used in the study[18] (4.75, 3.82, 2.86 and 5.04, respectively). The resulting theoretical values of Brønsted exponents are also summarized in Table I. As can be seen, the agreement between both sets of data is indeed very satisfactory.

Another example of widely investigated proton transfer processes is the ionization of nitroalkanes[22–30]. These systems are especially interesting since depending on the type of the catalyst, either the "ordinary" Brønsted plots with the exponent α in the range 0–1, or unusual plots with negative slopes (or the slopes exceeding unity) have been reported[31–35]. Thus while the ionization of nitroethane with a variety of amine bases[27,29] yields "normal" Brønsted plots with the exponent in the range 0.5–0.65, for the analogous ionization of a set of aliphatic nitroalkanes (nitromethane, nitroethane and 2-nitropropane) catalyzed by OH^- ions unusual plots with negative slopes are observed[31]. As it will be shown, the proposed approach is able to reproduce these experimental observations in both cases. Let us start first with the simpler "ordinary" case of the ionization of nitroethane catalyzed by the set of aliphatic amines[29]. Based on the experimental pK value of nitroethane (8.6) and the pK values of the amine catalysts, the straightforward calculation yields the value of the Brønsted exponent equal to

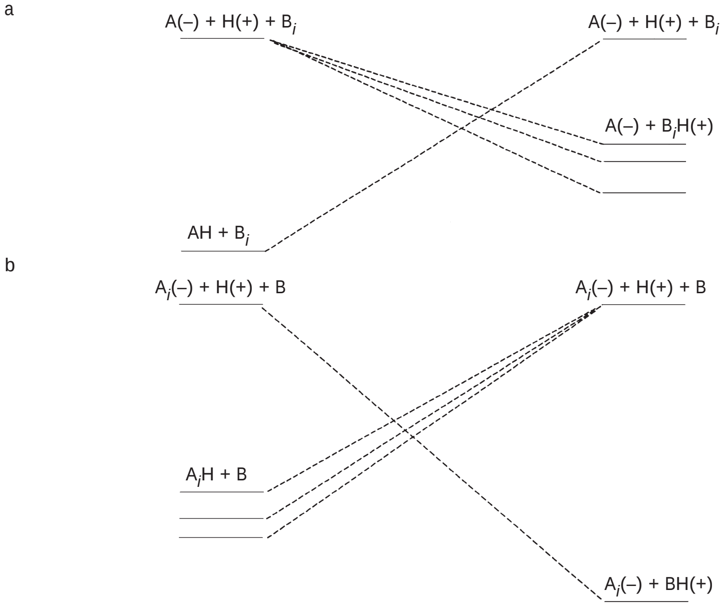
TABLE I
Experimental and calculated values of Brønsted exponents for the base-catalyzed bromination of carbonyl compounds

Molecule	pK	D_A	α_{exp}	α_{calc}	log R
3-Bromopentane-2,4-dione	7.0	9.6	0.42	0.39 ± 0.08	+2.04
Acetylacetone	8.9	12.2	0.52	0.48 ± 0.05	+1.54
Ethyl 2-oxocyclopentanecarboxylate	10	13.7	0.58	0.50 ± 0.07	+1.18
Ethyl acetoacetate	10.7	14.7	0.59	0.52 ± 0.07	+0.72
Ethyl 2-oxocyclohexanecarboxylate	11.9	16.3	0.67	0.55 ± 0.07	–0.99
Diethyl malonate	13	17.8	0.79	0.56 ± 0.07	–0.76
Chloroacetone	15.8	21.7	0.82	0.64 ± 0.06	–3.51
Acetone	19.3	26.5	0.88	0.68 ± 0.06	–6.78

0.52 ± 0.01 which is again in excellent agreement with the experimental value 0.50.

A reasonable agreement between theoretical and experimental Brønsted exponents can also be obtained for the bromination of nitromethane catalyzed by anions of aliphatic carboxylic acids. The experimental value of the exponent is 0.67 (overtaken from the study[23]), and the calculated value, based on the experimental p*K* of nitromethane, is 0.54 ± 0.11.

After having demonstrated the ability of the proposed model to reproduce reasonably the Brønsted exponents in "normal" cases, let us demonstrate now that the same approach is able to reproduce the experimental observations also in the case of unusual Brønsted plots. For this purpose let us discuss in more detail the dissociation of nitromethane, nitroethane and 2-nitropropane catalyzed by OH^- ions, for which unusual Brønsted plot with negative slope was reported[31]. In order to understand the origin of this unusual behavior, it is important to realize first the differences between these proton transfer reactions and the previous "normal" ones. Thus, for example, while in the case of "normal" plots a single C-acid reacted with a set of several base catalysts of moderate basicity, the situation in the "unusual" case is quite opposite and the set of several nitroalkanes reacts with a single base, whose basicity is extreme (OH^- ion). The above difference can be best demonstrated graphically in Scheme 3. The most impor-



SCHEME 3

tant difference which can immediately be seen in the scheme, and which also straightforwardly implies the differences in the slope of the corresponding Brønsted plots, is closely related to the reaction Gibbs energies. Thus while in the "ordinary" case the basicity of the amine catalysts was such that the whole process was endothermic, the extreme basicity of the OH^- ion leads, on the other hand, to the exothermic process. As a consequence of this change in the sign of ΔG^0, Eq. (*7*) can be rewritten as (*11*)

$$\overrightarrow{\Delta G^{\neq}} = \frac{D_A D_B}{D_A + D_B} - \frac{D_A \Delta G^0}{D_A + D_B}\,, \qquad (11)$$

from which the inversion of the sign of the Brønsted exponents is straightforwardly evident.

Using the experimental pK values of nitromethane, nitroethane and 2-nitropropane (10.2, 8.6 and 7.7, respectively), together with the pK of the OH^- ion (15.74 [20]), the calculated Brønsted exponent is indeed negative and its value is equal to –0.58 ± 0.05. We can thus see that the proposed approach is able to describe correctly the proton transfer reactions not only in "ordinary" cases, but also in cases where unusual Brønsted plots are observed. Despite this, there are, however, still some cases, whose explanation is puzzling. An example in this respect can be the studies[31–35] in which Brønsted exponents greater than 1 for the ionization of a set of substituted nitro(phenyl)alkanes catalyzed by OH^- ion were reported. Thus, for example, in the case of the substituted nitrophenylethanes[33], the unusual Brønsted plot was observed with the slope equal to +1.37. The possible origin of this unexpected result has been discussed[31–33], and although a tentative explanation has been offered in which the unusual slope was attributed to a greater sensitivity of proton removal by a base such as OH^- to substituent effect than in the case of the equilibrium constant, the satisfactory theoretical explanation of the phenomenon is still lacking.

In addition to allowing theoretical calculation of the Brønsted exponents, the proposed approach also straightforwardly explains the existence of the curvature in Brønsted plots. In this connection it is fair to say that the qualitative explanation of the curvature of these plots was possible also using the previous models[3,4,7,15], but while these models were able to reflect the existence of such a curvature as a general phenomenon, the quantitative estimate of whether or to what extent the deviations from the linearity can be important in any particular case was still out of the range of these models. Such a restriction does not exist in our approach which can be applied quite generally to any particular proton transfer process.

As an example of such an application, let us scrutinize in detail the dependences of calculated Gibbs energies of activation $\Delta G^{\neq}$ on the reaction Gibbs energies ΔG^0 for two particular reactions, namely the bromination of acetone and acetylacetone. The corresponding plots, based on the data of Bell[17–19], are given in Fig. 1. As can be seen, both curves significantly differ in the curvature of the plots. Thus, while in the case of acetone the curvature of the plot is relatively small, an analogous curve for acetylacetone is much more curved. Taking into account that the Brønsted exponent is defined as a derivative of $\Delta G^{\neq}$ with respect to ΔG^0, the small curvature of the dependence in the case of acetone allows to assume that relatively small deviations from linearity of the Brønsted plot can be expected over a relatively wide range of p*K*. On the other hand, in the case of acetylacetone, linear Brønsted plots can be expected only over a much narrower range of p*K*.

Another interesting application of the proposed approach concerns the possibility of its exploitation for the calculation of the activation Gibbs energies in a given proton transfer process, which can then be confronted with the actually measured reaction rates. An example of such a correlation based on the experimental data (log *R*) reported for the bromination of car-

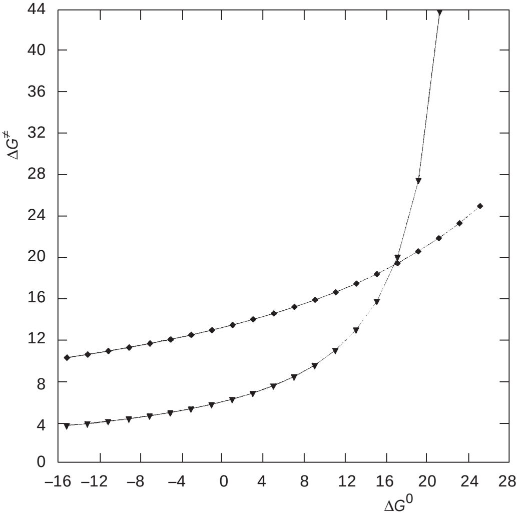


FIG. 1
Calculated dependence of activation Gibbs energies $\Delta G^{\neq}$ (in kcal/mol) on reaction Gibbs energies ΔG^0 (in kcal/mol) for the bromination of acetone (◆) and acetylacetone (▼)

bonyl compounds by Bell[17–19] is shown in Fig. 2. As can be seen, the agreement between the experimental reactivities (log *R*) and the calculated activation barriers is again very satisfactory.

Although the above examples clearly demonstrate that the proposed model is able to elucidate many features of proton transfer reactions, the applicability of this approach is even wider and allows also to rationalize some empirical rules and principles governing chemical reactivity in general. An example in this respect can be, e.g., the Hammond postulate[36].

This postulate, which relates the structure of the transition state to the Gibbs energy of the reaction ΔG^0, qualitatively measured by the exo- and/or endothermicity of the process, is often used as an important tool for mechanistic interpretation of Brønsted exponents as well as for discussion of the kinetic isotopic effects in these reactions. The proof of its validity could thus be of crucial importance for the reliability of the above mechanistic interpretations. In order to demonstrate the possibility of the theoretical justification of the Hammond postulate, it is useful to introduce the dimensionless quantity (*12*), which characterizes, within the proposed model, the relative position of the transition state on the reaction path (Scheme 2).

$$\frac{x^{\neq}}{a} = \frac{1}{2}\left(1 + \frac{D_{\mathrm{A}} - D_{\mathrm{B}}}{D_{\mathrm{A}} + D_{\mathrm{B}}}\right) \qquad (12)$$

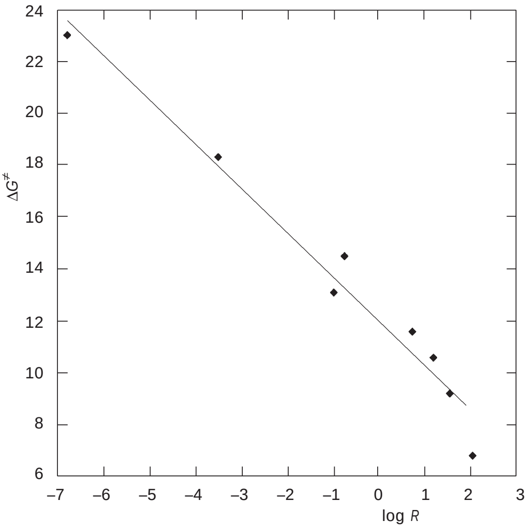


FIG. 2

Dependence of calculated activation Gibbs energies $\Delta G^{\neq}$ (in kcal/mol) on the experimental log *R* values for bromination of carbonyl compounds (r = 0.983)

Taking into account Eq. (*5*), Eq. (*12*) can be rewritten in the form (*13*),

$$\frac{x^{\neq}}{a} = \frac{1}{2}\left(1 + \frac{\Delta G^{0}}{D_{\mathrm{A}} + D_{\mathrm{B}}}\right), \tag{13}$$

from which the parallel between the position of the transition state on the reaction path and the exo- and/or endothermicity of the process is straightforwardly evident. Thus, for example, for exothermic reactions, characterized by negative values of ΔG^0, Eq. (*10*) leads to the value of the parameter $x^{\neq}a < 1/2$, which implies a reactant-like transition state. On the other hand, the same equation implies a product-like transition state ($x^{\neq}/a > 1/2$) for endothermic reactions.

CONCLUSIONS

A simple analytic model allowing to estimate the values of the Brønsted exponent in acid-base catalyzed reactions was proposed. The method is based on the simple idea of replacing the branches of intersecting potential energy curves by simple lines. Based on this assumption, the analytic formula for the Brønsted exponent could be derived which relates the values of this exponent to experimental p*K* values of the species participating in the given proton transfer process. The approach was tested on several series of acid-base catalyzed reactions and very satisfactory agreement with available experimental data was observed. The approach is applicable not only for reactions characterized by the "usual" values of the exponent lying within the range 0–1, but the correct description could also be obtained for reactions with unusual Brønsted plots with negative slopes. In addition to this, the model also provides simple theoretical justification for the validity of the Hammond postulate in proton transfer reactions.

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