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A New Approach to Analysis of the Nonlinearity of the Brønsted Relationship:

III.[1] An Empirical Procedure Combining the Method of σρ Correlations and the Concept of Hard and Soft Acids and Bases, as Applied to Normal CH Acids

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Abstract—A comparative σρ analysis was made of the experimental characteristics of the gas-phase (ΔG_{gas}), liquid-phase (pK_a), and kinetic ($\log k_D$) acidity of normal CH acids of various structures (terminal acetylenes, substituted benzenes, and methane derivatives CH_3X, CH_2X_2, and CH_2XY, where substituents X and Y are electron acceptors). The approach to interpretation of the correlation results took into account the concept of hard and soft acids and bases. The results of the σρ correlation analysis of ΔG_{gas}, pK_a, and $\log k_D$ of terminal acetylenes, allowing a common description of the effect of structural factors on these quantities with induction σ_I constants, suggest uniformity of the electronic interactions. As a consequence, there are no thermodynamic deviations from the Brønsted relationship. The correlations of ΔG_{gas} and pK_a of substituted benzenes, and also of methane derivatives forming nonplanar carbanions, suggest the prevalence of the induction effect on these quantities; however, the resonance effect makes an increased contribution to $\log k_D$. This difference in the behavior of the characteristics of the CH acidity is consistent with the conclusion made in the previous paper that the interactions in these compound series are characterized by solvation nonuniformity. For methane derivatives forming planar carbanions, the main mechanism of stabilization of these species in the gas phase, DMSO solution, and transition state of the reaction is the resonance effect. The experimentally observed deviation from the linearity of the Brønsted relationship is in this case also attributable to the nonuniformity of the interactions. The solvation interaction responsible for variation of pK_a in DMSO depends on the contributions of the electrostatic factor and H bonding, whereas the solvation interaction responsible for variation of $\log k_D$ involves only a certain fraction of the covalent bonding with a hydroxyl-containing solvent in the transition state of the reaction.

The Brønsted relationship as applied to CH acids is a typical correlation equation based on the linear relationship between the equilibrium constants (pK_a) and rates of deprotonation of the CH bond ($\log k_D$) in solution. Its importance is due to the fact that the Brønsted relationship, if valid in wide ranges of pK_a and $\log k_D$, furnishes information on the reaction mechanism. It was demonstrated previously by several examples that the Brønsted relationship is not always obeyed [2]. Restrictions imposed on the applicability of this relationship are associated with the structural features of CH acids and composition of the reaction medium; this is most often manifested in the curvature of the Brønsted plot and in strong deviations from the correlation, observed for certain CH acids. We noted previously [1, 3] that, when considering factors that affect deviations from the linearity of the Brønsted relationship, it is necessary to clearly distinguish the thermodynamic and kinetic deviations. It was noted that the thermodynamic deviations, despite their apparent significance, were not given due attention until recently, although physical interpretation of the Brønsted relationship could be insufficiently comprehensive without examining the role of the thermodynamic factor. Certain progress in this respect was provided by approaches based on the concept of two types of nonuniformity of interactions: solvation and intramolecular [1, 3]. The approach based on the concept of hard and soft acids and bases appeared to be a fairly simple and efficient way to reveal the solvation nonuniformity.

Analysis of the solvation nonuniformity, performed

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[1] For communication II, see [1].

within the framework of this approach, showed that deviations from the linearity of the Brønsted relationship (or their absence) are determined by whether the substances belong to normal and pseudo CH acids. The specific feature of normal acids is relatively frequent manifestation of the solvation nonuniformity in interaction of their carbanions with solvents. This nonuniformity is largely due to different solvation properties of solvents affecting pK_a (solvent DMSO) and $\log k_D$ (activation free energy of hydrogen isotope exchange, hydroxyl-containing solvents). More precisely, the solvation nonuniformity is due to hard electrostatic interaction of carbanions derived from normal acids with a polar aprotic solvent (DMSO), in contrast to less hard interaction of the "arising" carbanions (transition states in hydrogen isotope exchange) with a hydroxyl-containing solvent (alcohol, water). In contrast to normal CH acids, the solvating power of DMSO and hydroxyl-containing solvents toward both equilibrium carbanions of pseudo CH acids and transition states of reactions of pseudo CH acids appears to be fairly uniform, i.e., the medium in this case exerts no differentiating effect on the thermodynamic and kinetic CH acidity. Several examples demonstrate that pseudo CH acids obey the Brønsted relationship.

The conceptual approach based on solvation uniformity of interactions seems to be one-sided, since emphasis is made only on different external factors affecting pK_a and $\log k_D$, and the possible concomitant differences in the mechanism of the influence of intramolecular electronic effects are ignored. In this connection, we attempted to reveal the cases of intramolecular nonuniformity [1] by using the methods of σρ analysis. Preliminary examination of published data concerning applications of σρ analysis to studying various types of CH acidity also showed that pseudo and normal CH acids cannot be discussed from the same standpoint because of cardinal differences in the mechanisms of the transfer of structural effects to the reaction center. Therefore, in our previous paper [1] concerning the σρ analysis we considered pseudo CH acids only; their characteristic feature is significant delocalization of the electron density in the corresponding carbanions. We found that, among possible sets of σ constants of substituents, the only set ensuring adequate description of ΔG_{gas}, pK_a, and $\log k_D$ of pseudo acids is the so-called "three sigma" system suggested in [4]. It is a modified version of the system of nucleophilic σ_n^- constants, reflecting the prevalent effect of the direct polar conjugation between the central carbon atom and varied fragment of carbanions of CH acids. The fact that all the chosen objects are described by common correlations between pK_a or $\log k_D$ and σ_n^- constants (irrespective of the extent of substitution of the central carbon atom) allowed us to conclude that in these series of thermodynamic and kinetic CH acidity the interactions are uniform. Thus, we showed that in these series of CH acids there are no significant differences in the character of solvation and intramolecular interactions, although in other cases such differences may give rise to contradictions in interpretation of deviations from the Brønsted relationship.

For better understanding of the possibilities of the correlation approach to interpretation of deviations from linearity of the Brønsted relationship, we consider in this paper normal CH acids. In their carbanions, the electron density is mainly concentrated on the deprotonated carbon atom, with insignificant delocalization to other molecular fragments. To apply the previously used approach to normal CH acids, we systematically studied the correlations of ΔG_{gas}, pK_a, and $\log k_D$ with σ constants of substituents. It should be noted that it is difficult to clearly distinguish the effects of different electronic factors on these quantities. The main problem is to reduce the relatively complex, in the general case, set of intramolecular interactions (including, along with resonance and induction effects, also participation of *d* orbitals, interaction of nonbonded fragments, energy consumption for transformation of the starting CH acid into nonplanar carbanion, etc.) to one or two effects. In [1], to overcome the problem with correlation description of intramolecular interactions in pseudo CH acids, we distinguished the main electronic effect and neglected all the other effects, which led to somewhat rough results. In so doing, we based on the known analytical expression for the interaction energy given by MO LCAO method, according to which the effect of structural factors on the CH acidity may be associated with two types of interactions: orbital-controlled and charge-controlled. Examination of the experimental values of ΔG_{gas}, pK_a, and $\log k_D$ of pseudo acids showed that the case of the orbital control can be adequately described with modified nucleophilic σ_n^- constants. The same approach using the concept of hard and soft acids and bases allows us to distinguish the main type of intramolecular interactions in the opposite limiting case also, for normal CH acids, when the "pure" charge control takes place not only in equilibrium carbanions, but also in rigid, fully nonstabilized transition states of the reaction. In this simplest case we can neglect the contributions to the total interaction energy from all the electronic effects except the induction effect. In so doing, we hope to describe in a common form the effect of structural factors on ΔG_{gas}, pK_a, and $\log k_D$. If this is indeed possible, then the concept of hard and soft acids and bases, presented in the analytical form as in [1], can be used as an argument in favor of the uniform hard–hard interaction and hence in favor of linearity of the Brønsted plot. However, a nontrivial situation occurs when the charge formed on the deprotonated carbon atom in the transition state of the reaction is considerably lower than the charge on the same atom in the equilibrium carbanion. Since solvent molecules usually interact with both common and "arising" carbanions at the site of the highest electron density, it can be expected that factors determining the stability of equilibrium carbanions in DMSO differ in the electrostatic nature from the factors responsible for stabilization of the transition state of the reaction by specific interaction with alcohol or water molecules as hydrogen bond donors. The decreased hardness of the anionic center in the transition state of the reaction, as compared to the equilibrium carbanion, allows prediction of the possible intramolecular nonuniformity of interactions, which can lead to deviations from the linearity of the Brønsted relationship in accordance with our approach. Of course, this does not mean that the problem of choosing the optimal sets of σ constants when constructing the correlations for pK_a and $\log k_D$ has always the same solution. However, most probably, the inductive effect of substituents should be the most pronounced as far as variation of pK_a of normal CH acids corresponding to localized carbanions is concerned. At the same time, we must not rule out the possibility that the contributions of noninductive components of the total electronic effect to $\log k_D$ may increase to the level at which they cannot longer be neglected. We believe that it is objectively possible to obtain σρ correlations for $\log k_D$, but not for all normal CH acids, not with any high accuracy, and only within limited ranges of $\log k_D$.

To test these assumptions, we chose three classes of normal CH acids: terminal acetylenes, substituted benzenes, and some methane derivatives.

Terminal acetylenes. There are good grounds to class terminal acetylenes with normal CH acids. They form highly localized carbanions in which the degree of the *s* character of the orbital bearing the lone electron pair is 50%; proton transfer reactions involving these compounds are characterized by low activation barriers; proton abstraction from the CH bond occurs at a maximum possible rate for the given equilibrium constant, etc. [5]. Since the hardness of acetylenic CH acids, in terms of our approach, suggests the prevalence of the charge control in acid–base interactions, the correlation of pK_a, ΔG_{gas}, and $\log k_D$ with the inductive σ_I constants of substituents should be expected. Furthermore, according to classical electrostatic concepts, since the solvation stabilization of acetylenide carbanions in the gas phase is impossible, the negative charge on the anionic carbon atom in the gas phase should be higher than in the liquid phase, and hence ΔG_{gas} should be the most sensitive to the inductive effect of substituents [3, 5]. However, at present, the correlation of ΔG_{gas} with σ_I constants can be checked with only a limited set of compounds. These include CHCH, C_6H_5CCH, p-$CH_3C_6H_4CCH$, CH_3CCH, $ClCH_2CCH$, CH_3COCCH, and $CH_3OCO \cdot CCH$ [6, 7]. The correlation that we obtained, indeed, indicates that the inductive effect on ΔG_{gas} prevails and that this quantity is very sensitive to the inductive effect of substituents in terminal acetylenes (correlation for reaction series I, see table). Experimental study of the electronic effects of substituents on pK_a in terms of σρ analysis is complicated by the fact that the pK_a values for the majority of compounds of this series, measured in DMSO, differ by no more than 1–2 units. This very narrow range of pK_a variation, determined by the presence at the C≡C bond of only weak acceptor substituents, does not allow us to reliably determine with what set of σ constants the pK_a values correlate. We performed the σρ analysis of pK_a with a set of CH acids XC≡CH including the acids with polar substituents X {$CH_3CH_2CH_2S$, $(C_2H_5)_3Si$, C_6H_5, CH_3OCH_2, $(CH_3)_2NCH_2$ [8]}. Also, to extend the range of variation of pK_a toward low pK_a values, we included ethynyl-substituted six-membered nitrogen heterocycles: 2- and 4-ethynylpyridines [9]. The pyridyl fragments are strong electron acceptors by the inductive mechanism. Their σ_I constants (for DMSO solutions) are 0.21 (2-pyridyl) and 0.43 (4-pyridyl) [10]. From these data, we obtained a linear correlation of pK_a with σ_I constants (series II).

Previously, when analyzing differences in the electronic interactions affecting ΔG_{gas}, pK_a, and $\log k_D$ of pseudo CH acids, we gave major attention to comparison of the reaction constants ρ characterizing the sensitivity of these quantities to the prevalent electronic effect [1]. To make sure whether the ρ_I constant of the correlations for terminal acetylenes varies in going from the gas phase to DMSO solution significantly or insignificantly, it is appropriate to include in analysis also OH acids XOH (X is a varied substituent) for which the prevalence of the inductive effect on pK_a(gas) and pK_a was proved previously [11]. Solvation of OH acids in DMSO was judged in [11] from the ρ_{gas} and ρ_{DMSO} values, which proved to be 7.0 and 4.6, respectively. The table shows that the related constants ρ for the series of terminal acetylenes are 59 and 9. The similar decrease in the sensitivity constants in going from the gas phase to solution suggests that the nature of solvation is similar in

$\sigma\rho$ Correlations of the free energies of the gas-phase reactions (ΔG_{gas}, kcal mol^{-1}), acid dissociation constants in solution (pK_a), and logarithms of the rate constants of hydrogen exchange ($\log k_D$) of normal CH acids[a]

Series no.	Class of correlated CH acids	Correlation equation	*r*	*s*	*N*[b]
I	Terminal acetylenes	$\Delta G_{\text{gas}} = -59\sigma_I + 369$	0.091	1.1	7
II	″	$\text{p}K_a = -9.0\sigma_I + 31$	0.980	0.30	8
III	″	$\log k_D = -8.6\sigma_I + 1.44$	0.972	0.39	14
IV	*o*-Substituted benzenes and aromatic heterocycles	$\Delta G_{\text{gas}} = -27\sigma_I + 391$	0.989	0.79	8
V	*o*-Substituted benzenes and five-membered aromatic heterocycles	$\text{p}K_a = -12\sigma_I + 43$	0.945	1.1	8
VI	1- and 1,3-Disubstituted benzenes	$\log k_D = 7.2\Sigma\sigma_I + 0.8\Sigma\sigma_R - 9.4$	0.998	0.32	10
VII	Mono- and various disubstituted benzenes	$\log k_D = 7.2\sigma_I^o + 0.8\sigma_R^{-o} + 4.4\sigma_I^m + 1.7\sigma_R^{-m} + 3.2\sigma_I^p + 2.9\sigma_R^{-p} - 9.4$	0.998	0.73	16
VIII	Substituted methanes of the first structural group	$\Delta G_{\text{gas}} = -57\sigma_I + 394$	0.992	2.1	8
IX	″	$\text{p}K_a = -49\sigma_I + 57$	0.992	1.3	8
X	Substituted methanes of the second structural group	$\Delta G_{\text{gas}} = -45\sigma_{\text{CH}_n^-} + 404^c$	0.956	0.20	9
XI	″	$\text{p}K_a = -22\sigma_{\text{CH}_n^-} + 47^c$	0.997	0.18	16
XII	″	$\log k_D = 7.9\sigma_{\text{CH}_n^-} - 16.0^c$	0.987	0.19	8

[a] For the names or structural formulas of the CH acids under consideration, reaction media in which pK_a and $\log k_D$ were measured, and temperatures of kinetic experiments, see text. [b] (*N*) Number of correlated points. [c] $n = 3$ or 2 for methyl-substituted CH acids and alkylaromatic hydrocarbons, respectively.

both cases. Following the conclusions made in [11], we have good grounds to state that the strong weakening of the substituent effects on pK_a is mainly due to electrostatic solvation of acetylenide ions in an aprotic solvent.

Passing to comparative consideration of variations in the equilibrium constant of deprotonation in solution (pK_a) and rate constant of hydrogen exchange ($\log k_D$), we can note that a large body of experimental data is available on $\log k_D$, but these data, unfortunately, cannot be directly correlated with the available data on pK_a. The most complete are data on the kinetics of hydrogen exchange of terminal acetylenes in aqueous buffer solutions containing OH^- ions (25°C) [12]. The range of the measured rates in the reaction series under consideration covered seven orders of magnitude. The names of the CH acids studied and the $\log k_D$ values are listed in [12] and are not given here. Kresge and Powell [12] concluded that the resonance effect of substituents does not make noticeable contribution to the reactivity of the examined CH acids. The linear correlation of $\log k_D$ with the inductive σ_I constants, found in [12], has the form given in the table (reaction series III). Comparison of the reaction constants ρ_I for series III and II shows that the sensitivity of $\log k_D$ to the inductive effect is approximately equal to that in the series of liquid-phase thermodynamic CH acidity: $\rho_I(\log k_D)/\rho_I(\text{p}K_a) \approx 1$. In view of the above reasoning, this fact suggests chage control of interactions between the transition state in aqueous solution and solvent molecules. Thus, on the whole, in both systems compared a uniform hard–hard interaction occurs, and the linearity of the Brønsted relationship is preserved.

Let us discuss whether the $\rho(\log k_D)/\rho(\text{p}K_a)$ ratio can characterize the position of the transition states on the reaction coordinate (as reaction coordinate we take the degree of transformation of the starting CH acid into the carbanion). We should primarily note that the coefficient α of the Brønsted correlation, obtained from the kinetic data in aqueous solutions and equilibrium data in DMSO, is close to unity [13]. This means that the transition state should be strongly shifted toward the reaction products. The fact that α is equal to $\rho(\log k_D)/\rho(\text{p}K_a)$ indicates that this ratio can be used as an independent test for estimating the degree of cleavage of the CH bond in the transition state of the reaction. The fact that the kinetic isotope effect in hydrogen exchange of substituted acetylenes is close to unity ($k_D/k_T \approx 1$) [13] also deserves attention. This result, confirming that the CH acids under consideration can be classed with normal acids, indicates that the reaction rate is controlled by the step of diffusion of the reaction products [14].

***o*-Substituted benzenes and related compounds.** *o*-Substituted benzenes and their heterocyclic analogs (pyridines, thiophenes, furans) are attractive objects for comparative σρ analysis of various types of acidity of normal CH acids. Changes in the rate and mechanism of deuterium exchange occurring upon variation of the structure of the aryl moiety, provided that the aromatic CH bond remains the reaction center, were extensively discussed in the literature (see, e.g., [15, 16]). At the same time, data on combined σρ analysis of ΔG_{gas} and pK_a values of substituted benzenes and aromatic heterocycles are still lacking. Prior to presenting the results of our treatment, we should note that combination of benzenes and aromatic heterocycles in common reaction series involves certain problems, since the σ_I constants of heteroaromatic fragments considered as substituents depend on the reaction medium and choice of the standard reaction series [17]. To construct correlations for pK_a and ΔG_{gas}, we took advantage of the value of σ_I(2-pyridyl) 0.21, corresponding to the reaction in DMSO [17], and of the maximal values among those published for 2-thienyl (σ_I 0.8) and 2-furyl (σ_I 0.7) [18]. Available data on ΔG_{gas} concern the following compounds with a substituent in the *o*-position relative to the acid center: C_6H_6, C_6H_5F, C_6H_5Cl, $C_6H_5CF_3$, C_6H_5CN, thiophene, pyridine, and naphthalene [19, 20]. As seen from the table, for these compounds ΔG_{gas} correlates with σ_I with a high quality of the correlation (reaction series IV). Hence, in the series of gas-phase CH acidity of *o*-substituted benzenes, as in the similar series of terminal acetylenes (series I), the inductive effect essentially prevails over the resonance effect.

Data on pK_a values of *o*-substituted benzenes and aromatic heterocycles are scarce; these values were mainly measured in tetrahydrofuran [21–23]. The objects of our consideration were the below-listed very weak CH acids characterized, nevertheless, by a wide range of variation of the liquid-phase CH acidity [21, 22]: C_6H_6, $C_6H_5OCH_3$, $C_6H_5N(CH_3)_2$, $C_6H_5OC_6H_5$, C_6H_5CN, $C_6H_5C{\equiv}CC_6H_5$, thiophene, and furan. It should be noted that not all the pK_a values that we used are equally reliable. According to [23], this mainly concerns $C_6H_5N(CH_3)_2$ whose acid properties are extremely weak. The insufficient reliability of description of the inductive effect of heteroatomic grops using σ_I constants is apparently responsible for certain scattering of points about the regression straight line in construction of the pK_a–σ_I correlation; as a result, the correlation coefficient is relatively low. Nevertheless, the correlation does exist (series V). The sufficient reliability of the correlation for series V is indicated, in particular, by the fact that the absolute term in this reaction series (pK_0 43) is close to pK_a of the "parent" compound, benzene, obtained by extrapolation, based on the additivity principle, of the pK_a values of polyfluorinated benzenes, measured in tetrahydrofuran (THF): pK_a(C_6H_6) 44.8 [21]. It is also close to pK of benzene in cyclohexylamine, estiated similarly: pK(C_6H_6) 43 [24].

The equation parameters for series V indicate that, despite relatively low quality of the correlation, pK_a of the examined series of benzenes is extremely sensitive to the inductive effect of substituents (ρ_I 12). At the same time, as judged from pK_a of monohalosubstituted benzenes C_6H_5X (X = Cl, F), these compounds do not obey the calculated equation for series V. Our attempt to assess the electronic effect on pK_a for the whole series of *o*-substituted benzenes by using other types of σ constants (resonance σ_R constants and also σ_α constants taking into account additional stabilization of carbanions due to electrostatic interaction between the charge of the reaction center and the induced dipole of substituents) failed.

It should be noted that the σρ correlation analysis of pK_a can also be applied to polyhalo-substituted benzenes. Indeed, as shown in [21], successive increase in the number of chlorine atoms introduced into the benzene molecule results in progressing enhancement of the acid properties of the compounds. The influence of chlorine (and also fluorine) atoms is additive and is apparently due to their inductive effect. Satisfactory correlation pK_a–σ_I is attained with the following compounds included in the reaction series: C_6H_5Cl, 1,3-$C_6H_4Cl_2$, C_6H_5F, 1,3-$C_6H_4F_2$, and also unsubstituted benzene (pK_a 47) [21].

The linear dependence thus obtained has the same slope (ρ_I 11.7) as the dependence valid for monosubstituted benzenes (series V), but the absolute terms are different. We believe that the coincidence of the numerical values of ρ gives certain insight into the causes of subdivision of the whole set of substituted benzenes into groups. Namely, although the effect of THF on pK_a is complex and is governed by factors determined by the properties of both CH acid and solvent, subdivision of the benzenes under consideration into two groups is most likely due to the specific differentiating effect of THF on carbanions derived from halobenzenes.

The above approach to estimating the degree of solvation of acetylenide carbanions, based on comparison of ρ_I(gas) and ρ_I (series II, I) was applied by us to esimating the solvating power of THF toward phenide anions $XC_6H_4^-$. If, as in series I and II, we use the quantity pK_a(gas) = $\Delta G_{gas}/RT$ to make the correlations describing pK_a in the gas phase (series IV) and in THF solutions (series V) comparable, we obtain a decreased slope of the straight line for pK_a(gas): ρ_I 20. Comparison with the data for series I and II shows that interaction of phenide anions with THF results in considerably less pronounced (by a factor of ~3) weakening of the substituent effects as compared to the weakening caused by solvation of acetylenide ions in DMSO. The relatively small narrowing of the scale of equilibrium acidities of substituted benzenes in THF is apparently due to the effects of interionic interactions in low-polarity THF. In particular, it may be due to decreased charge on the carbon atom of the deprotonated CH bond in phenide anions, compared to acetylenide anions.

Detailed σρ analysis of data on the deprotonation kinetics of substituted benzenes was repeatedly performed previously, including examination of their Brønsted behavior [15, 25]. The solvent systems mainly used as reaction media were characterized by high thermodynamic basicity: solutions of potassium amide in liquid ammonia, of lithium and cesium cyclohexylamides in cyclohexylamine, and of potassium dimsyl and *tert*-butylate in DMSO. In all the systems, the predominant contribution of the inductive effect of the *o*-substituent was found, with the sensitivity constants ρ_I approximately corresponding to the constant ρ_I 12 initially obtained for the system KNH_2–NH_3(liq) [15]. Our interest was primarily focused on a considerably less basic solvent system, sodium methylate–methanol (pK_{BH} 15.5). This system is attractive because of relatively soft solvation interaction of normal CH acids with the protic solvent, in contrast to considerably harder interactions in highly basic aprotic media (pK_{BH} ~40–42). This nonuniformity gives rise to deviations from the linearity of the Brønsted relationship [3].

The pattern of electronic interactions following from the results of kinetic studies of hydrogen exchange of *o*-substituted benzenes in alcohol is qualitatively similar to the pattern following from data on pK_a and ΔG_{gas}, but differs quantitatively, as will be shown below. In particular, we found in [26] that the correlation characterized by the equation of series VI is obeyed in a very wide range of the rates of hydrogen exchange in mono- and 1,3-disubstituted benzenes with a solution of sodium methylate in methanol (140°C). Along with relationship VI valid for hydrogen isotope exchange in monosubstituted benzene and also in 1,3-disubstituted benzenes (for 2-position), we obtained in [26] multiple correlation VII for disubstituted benzenes describing also the mechanism of the electronic effects when the second substituent is in the remote (*m*- or *p*-) position relative to the reaction center. Comparison of the results of extended σρ analysis (relationships VI and VII) shows that variation of the position of the second substituent does not cause variation of the sensitivity constant ρ_I^o 7.2 in correlation VII, compared to ρ_I^o in correlation VI. That is, the inductive contribution to $\log k_D$ made by an *o*-substituent in mono- and various disubstituted benzenes is approximately constant.

In contrast to series IV and V of thermodynamic CH acidity, in which the inductive effect of substituents essentially prevails over the resonance effect, in series VI and VII of the kinetic CH acidity the resonance effect makes a more significant contribution. In terms of σρ analysis, this is manifested in successive growth of ρ_R at the expense of a decrease in ρ_I with increasing distance between the substituent and reaction center; for the *p*-H atoms, the constants ρ_i and ρ_R become comparable.

It should also be noted that the secondary resonance effects in *m*- and *p*-substituted benzenes are also manifested in deuterium exchange in a highly basic system, solution of potassium amide in ammonia [25].

Comparison of the correlation equations obtained for pK_a and $\log k_D$ shows that, although the character of the prevailing electronic effect is preserved in going from the equilibrium to kinetic CH acidity, in the latter case the inductive effect of substituents is largely weakened, and the resonance effect becomes more significant. This can be considered as manifestation of the intramolecular nonuniformity of the interactions, with which deviations from the linearity of the Brønsted relationship can be quite pronounced [3].

As in the case of other classes of CH acids, it seems important to follow the relationship between the ratio $\rho(\log k_D)/\rho(pK_a)$ and the coefficient α of the Brønsted relationship, i.e., between the parameters that can potentially characterize the position of the transition state on the reaction coordinate. It should be noted here that the published estimate of the Brønsted coefficient α is doubtful or, at least, very approximate [27]. Indeed, the linear correlation between $\log k_D$ and pK_a was built only for fluorobenzenes and was based on only four points, including points for fluorinated benzenes in which the substituent F is remote from the CH bond being deprotonated. Furthermore, $\log k_D$ and pK_a were determined with a relatively large error, since they were obtained from $\log k_D$ and pK_a of polyfluorobenzenes using an approximate additive scheme. Although the range of variation of $\log k_D$ and pK_a is fairly wide, a monotonic increase in $\log k_D$ with decreasing pK_a, in our opinion, cannot be a good reason for correct determination of α. The value of α 0.92 obtained in [27] contradicts the value of α 0.6 equal to the ratio $\rho(\log k_D)/\rho(pK_a)$ derived from correlations V and VI, or V and VII. The above data should be certainly taken into account when interpreting the character of interactions responsible for variation of pK_a and $\log k_D$ of substituted benzenes. If the coefficient α should be close to unity accorting to [28], then the pattern of these interactions should be similar to that discussed above for terminal acetylenes, i.e., it should be based on the diffusion exchange mechanism. In this case, the uniform hard–hard interaction is inevitably realized, and the Brønsted relationship is obeyed. On the contrary, ionization of CH acids forming a Brønsted dependence with $\alpha \sim 0.5–0.7$ involves a relatively "late" product-like transition state, with relatively weak effect of the diffusion step on the reaction rate.

Certain published data cast doubt on the possibility of adequately characterizing the properties of the transition state by the value of α in all cases. An alternative parameter is the primary kinetic isotope effect of a reaction (k_D/k_T ratio). In isotope exchange of benzene and its derivatives with liquid ammonia in the presence of KNH_2, with cyclohexylamine in the presence of lithium cyclohexylamide, and with DMSO in the presence of potassium dimsyl, the k_D/k_T ratios were in the range 2.0–3.0 [28], consistent with the mechanism in which the rate-determining stage is proton detachment from the CH acid in its reaction with a base. Furthermore, in agreement with the theoretically expected trends in variation of k_D/k_T for reactions in the lithium cyclohexylamide–cyclohexylamine system without diffusion control, k_D/k_T grows with decreasing pK_a. The k_D/k_T ratio for unsubstituted benzene-*D*(*t*) ($pK_a \sim 43$) noticeably differs from unity (k_D/k_T 1.6), and in going to fluorobenzene-2*D*(*t*) (pK_a 37.3) it approaches the theoretical limit of ~3 [29, 30].

On the whole, the trend in variation of k_D/k_T corresponds to the intermediate value of α between 0 and 1; hence, the conclusion made in [28] that the true value of α is close to 1 is subject to objections. At the same time, it seems true that the ratio $\rho(\log k_D)/\rho(pK_a)$ is in this case a preferable criterion of the extent of proton transfer from a CH acid to a base in the transition state. This standpoint, which may also be open to question, can be substantiated as follows. According to [3], common application of the Brønsted relationship to a wide range of normal CH acids does not give satisfactory results. Indeed, previously we combined the sets of $\log k_D$ and pK_a data for normal CH acids that have certain common features but different structures (fluorinated benzenes, five-membered aromatic heterorings, nitrocyclopropane, cyclopentadiene, indene) and attempted to perform their combined treatment with the aim to obtain a common Brønsted relationship. We found that the above normal CH acids do not obey a linear relationship in the coordinates $\log k_D–pK_a$. The lack of correlation was explained by the fact that the carbanion in DMSO is stabilized by hard electrostatic interaction of the central carbon atom bearing the localized charge with the solvent molecules. At the same time, the transition state of the corresponding reaction in alcohol is more similar in hardness to pseudo CH acids, as it is mainly solvated in the covalent fashion with formation of hydrogen bonds. Nonuniform solvation of the long-lived carbanion and reaction transition state makes it necessary to subtract by a specific procedure the contribution of electrostatic solvation from pK_a. Using the corrected values of pK_a^{cor}, i.e., the experimental values of pK_a of normal CH acids minus the contribution of electrostatic solvation, we determined that linear correlation between pK_a^{cor} and $\log k_D$ is valid, with the Brønsted coefficient α' of the modified dependence $\log k_D = \alpha' pK_a^{cor} + b$ equal to 0.4.

Substituted methanes. Application of $\sigma\rho$ analysis to substituted methanes was attempted for a long time [4, 31, 32]. We believe that the problems with correlation analysis of the CH acidity of these compounds can be overcome only after revision of the existing views considering the whole set of substituted methanes as a common structural series [4, 31, 32]. It should be borne in mind that the specific features of the kinetic and equilibrium behavior of substituted methanes as CH acids are primarily determined by the structural features of the corresponding carbanions (the structural effects in the initial CH acids are considered to be insignificant). For the majority of compounds of this class, the actual configurations of the carbanions in the gas phase are unknown, but for any not very complex substituted methanes the geometries of the carbanions can be calculated fairly accurately and unambiguously by methods of quantum chemistry. Specifically this fact allows methane derivatives containing acceptor substituents to be subdivided into separate structural groups. Apparently, the best solution for the $\sigma\rho$ analysis of ΔG_{gas}, pK_a, and $\log k_D$ of a large set of substituted methanes is subdivision of these compounds into two groups. The first group includes mnethanes containing tetrahedral substituents: $(CH_3)_2S$, $(CH_3)_2SO$, $(SH_3)_2SO_2$, $C_6H_5SH_3$, $CH_3SO_2C_6H_5$, CH_3CH_3, $(CF_3)_2CH_2$, and also CH_3CN and $CH_2(CN)_2$. In the context of our discussion, taking into account the nonplanar configuration of the carbanions of these CH acids, it is appropriate to consider the correlation of the acidity characteristics with the inductive constants of substituents σ_I.

The second structural group includes a large number of compounds containing a CH_3 or CH_2 group as acid center (CH_3X, CH_2X_2, CH_2XY), in particular, monosubstituted compounds CH_3NO_2, $C_6H_5CO \cdot N(CH_3)_2$, CH_3COCH_3, $C_6\mathit{H}_5COCH_3$, $CH_3COOC_2H_5$, CH_3CN, and $C\mathit{H}_3SO_2C_6H_5$, and disubstituted compounds $CH_2(CN)_2$, $C\mathit{H}_2(COOC_2H_5)_2$, $(CH_3SO_2)_2C\mathit{H}_2$, $C_6H_5C\mathit{H}_2COC_6H_5$, $(C_6H_5S)_2C\mathit{H}_2$, $(C_6H_5SO_2)_2C\mathit{H}_2$, $C_6H_5SC\mathit{H}_2COOC_2H_5$, $C_6H_5C\mathit{H}_2CN$, $CH_3SC\mathit{H}_2CN$, etc. Despite the lack of direct experimental evidences, the majority of researchers believe that the planar configuration is the most favorable for the carbanions derived from these acids, as it ensures the maximal overlap of the *p* orbital of the anionic carbon atom with the π orbital of the carbonyl, nitro, or other strong acceptor group and localization of the negative charge to a greater extent on the peripheral atoms [33]. High-level *ab initio* calculations of the carbanions derived from the simplest representatives of these acids, CH_3NO_2 and $(CH_3)_2CO$, also suggest the planar structure of the carbanions [34]. The correlations of ΔG_{gas}, pK_a, and $\log k_D$ with the substituent σ constants are considered below as applied to each structural group of substituted methanes separately. Before discussing the results of the correlation analysis, we should note that the ΔG_{gas} values for methanes of both groups are summarized in [35–37], and the pK_a values, in [38, 39].

First structural group. As we expected, the correlations of ΔG_{gas} and pK_a are attained with σ_I constants of the substituents or with the sums of these constants (series VIII and IX). The high sensitivity constant, ρ_I 57, of correlation VIII for methane in the gas phase, as in the case of terminal acetylenes (correlation I), apparently indicates that in the carbanions the major part of the negative charge remains on the deprotonated carbon atom retaining the pyramidal structure. Neglecting the differences between the ρ_I values given in the table, we can state that the methyl anions of the first group should be similar to acetylenide anions in the degree of the charge localization on the anionic carbon atom and in its distribution over the remaining atoms. In both reaction series, the process is charge-controlled. At first glance, this conclusion can be refuted by an apparent inconsistency between the drastic decrease in ρ_i in going from the gas phase to DMSO solution in the acetylene series (series I and II) and the lack of any variation of ρ_I when similar transition is made for the CH acids under consideration (correlations VIII and IX) {note that, when comparing the sensitivity constant ρ_I for the free energy ΔG_{gas} with that for pK_a, it is necessary to pass from ΔG_{gas} to $pK_a(gas) = \Delta G_{gas}/1.37$; then $\rho_I[pK_a(gas)]$ becomes equal to 42 (series VIIIa)}.

To understand the causes of this anomaly, it is appropriate to consider the quantum-chemical data for carbanions of this type. These data show that such carbanions are characterized by a strained configuration due to strong intramolecular Coulomb interaction [40, 41]. The *ab initio* calculations were made with the CH acids $(CH_3)_2S$, $(CH_3)_2SO$, and $(CH_3)_2SO_2$ [40, 41]. According to the conclusion made in [40, 41], the key role in stabilization of the carbanions of these sulfur-containing CH acids is played by intramolecular purely electrostatic attraction between the methylene group CH_2^- as electron-excessive center and the sulfur atom in the carbanion, charged more positively. The occurrence of this attraction is suggested, in particular, by an essentially shortened distance between the S and C^- atoms, given by calculations; the extent of shortening of this distance relative to the sum of the atomic radii grows in the order S < SO < SO_2. The shortening of the distance between the electrostatically interacting atoms is itself an indirect evidence that the solvent effect on the transfer of electonic effects in these carbanions is weakened. This can be illustrated by data available for certain molecular systems. For example, interactions between very closely located fragments in 1,8-disubstituted naphthalenes [42] and *o*-disubstituted benzenes [43] depend on the medium very weakly. The conclusion that the effect of solvation on the state of carbanions under consideration in DMSO is weak can also be made on the basis of an electrostatic model assuming that the intermolecular interactions in a field produced by a polar aprotic solvent are essentially different in cases when oppositely charged atoms in carbanions are at different distances from each other. Namely, in the extreme case when the distances between the DMSO molecules and centers of localization of the opposite charges in a carbanion exceed by an order of magnitude the distance between these centers, we can speak of interaction of solvent dipoles with a very short dipole (point approximation), rather than of interaction of solvent dipoles with discrete charges in the carbanion separated from each other by a long distance. The intensity of the field produced by a very short dipole and the energy of interactions involving it decrease with the distance much faster than the related characteristics of charges separated by a long distance.

In the case of methanes of the first group, the specific features of electronic interactions affecting $\log k_D$ can be elucidated by comparing the correlations for pK_a and $\log k_D$. However, because of the small number of the measured $\log k_D$ values, a correlation between $\log k_D$ and σ constants in the strict sense cannot be obtained. By now, the kinetics of hydrogen exchange has been studied experimentally only for four compounds of this group, listed below (in parentheses are given the $-\log k_D$ values obtained in the catalytic system $C_2H_5OK–C_2H_5OH$ at 0°C: $(CH_3)_2SO$ (7.9), $CH_3SOC_6H_5$ (7.2), $(CH_3)_2SO_2$ (4.0), $4\text{-}NO_2C_6H_4 \cdot SO_2CH_3$ (2.3) [44, 45]. No linear correlation is found between these $\log k_D$ values and inductive σ_I constants of the substituents, i.e., the inductive effect is not decisive in this case. At the same time, there is almost linear correlation of $\log k_D$ with the modified nucleophilic Kabachnik constants σ_n^- [4]; the correlation, if it indeed takes place, is characterized by $\rho_n^- \sim 14$. Hence, the intramolecular interactions governing the variation of the kinetic CH acidity of methanes of the first structural group differ essentially from the intramolecular interactions responsible for their equilibrium CH acidity in DMSO. Irrespective of the specific cause of this difference between the correlations for pK_a and $\log k_D$, this fact is of interest, because the pattern is qualitatively similar to that observed with the other class of normal CH acids, substituted benzenes. In the case of substituted methanes of the first group, the difference between the $\sigma\rho$ correlations for pK_a and $\log k_D$ is even considerably more pronounced. The different character of the correlations strongly suggests that, if a large set of kinetic data will be obtained, attempts to achieve linearity of the Brønsted relationship between pK_a and $\log k_D$ will fail. Indeed, as in the other reaction series analyzed above, passing from the gas phase to a DMSO solution does not lead in this case to deformation of the electronic shells of the carbanions and solvent molecules. Therefore, variations of pK_a values determined by solvation of the corresponding equilibrium carbanions are charge-controlled (inductive stabilizing effect). On the contrary, carbanions in the transition state in an alcoholic solution do not show large similarity with the “free” carbanions in DMSO. Solvation of the transition states by hydrogen bonding with the solvent affects their electronic structures, shifting the electron clouds from the atom with the highest electron density to alcohol molecules. Planarization of the reaction transition states in alcoholic solution, accompanying relaxation of the electron density, suppresses the contribution of the inductive effect to $\log k_D$, increasing thus the contribution of the resonance effect.

Methanes of the second structural group. Application of the $\sigma\rho$ correlation approach to the reaction series of CH acidity of methanes that form planar carbanions upon deprotonation involves certain problems. The point is that the principal idea of our approach is based on the concept that deprotonation of normal CH acids is charge-controlled; hence, according to the quantum-chemical substantiation of the concept of hard and soft acids and bases, the inductive effect of substituents should exert a decisive influence on ΔG_{gas} and pK_a of such CH acids. Classification of methanes of the second groups with normal CH acids is supported by a number of facts (see, e.g., [5, 46]); we will not discuss them in this paper. Such classification can be additionally supported by the lack of linear correlation between pK_a(DMSO) and $\log k_D(H_2O)$, with the fulfillment of the Brønsted relationship with pK_a^{cor} taken instead of pK_a(DMSO) [3]. From the viewpoint of applying the principle of hard and soft acids and bases, it remains unclear why the correlations for ΔG_{gas} and pK_a of the above-named methanes can be obtained with nucleophilic Kabachnik constants $\delta_{CH_n^-}$ only [4], as these constants take into account direct polar conjugation of a substituent with a carbanionic reaction center (series X and XI). For understanding the cause of unusual, for normal acids, correlation of ΔG_{gas} or pK_a with the σ_n^- constants, it is important that the parameters of correlations X and XI closely coincide with those found for pseudo CH acids (*p*-substituted toluenes, polynuclear unsaturated carbocycles, arylacetonitriles) [1]. In particular, the ρ_n^- constants of the correlations for arylacetonitriles, $\rho_n^-(\Delta G_{gas})$ 51 and $\rho_n^-(pK_a)$ 22, as well as their free terms, $\Delta\Delta G^0_{gas}$ 400 and pK_a^0 47 [1], virtually coincide with the ρ_n^- constants and absolute terms in correlations X and XI. The fact that correlations X and XI, obtained for substituted methanes of the second group in the gas phase and DMSO, are virtually identical to the similar correlations found for the above-mentioned pseudo CH acids can be attributed to relatively weak solvation of anions of these CH acids in solution. The specific features of the equilibrium behavior of these CH acids are due to strong electron-acceptor power of the varied molecular fragments adjacent to the carbon atom being deprotonated. In equilibrium carbanions, a significant fraction of the negative charge is shifted to these fragments. According to ^{13}C NMR data for solutions of substituted alkyl anions of this type in DMSO, only 0.4 – 0.5 of the carbanion charge remains on the anionic carbon atom [31, 32], i.e., the extent of the electron density delocalization is close to the limiting values corresponding to the structures of anions of alkylaromatic hydrocarbons and their derivatives. Hence follows that the effect exerted by electrostatic solvation of carbanions derived from both series of CH acids with DMSO molecules is similar in the nature and value.

From the viewpoint of statistical treatment, the situation with $\log k_D$ data for methanes of the second group is more favorable compared to the first group. We will, however, consider only a limited number of CH acids of the second group, for which the kinetic characteristics were obtained in water at 25°C, with the H_2O molecule being the only base in the system.

The names of these CH acids and the corresponding $\log k_D$ values, as well as the pK_a values measured in DMSO, are given in [3]. The use of these substituted methanes as objects of correlation analysis is also attractive because of the deviations from the linearity of the Brønsted relationship, observed with these compounds. The kinetic data obtained in water are described by relationship XII with nucleophilic σ_n^- constants, i.e., as in the series of the equilibrium acidity of methanes of the second group, the resonance effect is the main mechanism of carbanion stabilization in the reaction transition state. Following the same approach as in the case of the CH acids considered above, we discuss below why methanes of the second group show deviations from the "normal" Brønsted behavior, despite the fact that both pK_a and $\log k_D$ are mainly influenced by the same resonance effect. The key point of our approach is that the transition state differs from both the initial CH acid and the final carbanion in the nature of solvation interactions and in the atomic charges. Presumably, if deprotonation of these CH acids occurred in the gas phase, rearrangement of the initial state of the CH acid in the transition state would be far from completion, the structure of the central carbon atom would be close to pyramidal, and the extent of charge delocalization would be intermediate between weak delocalization in the initial molecule and maximally strong delocalization in the planar equilibrium carbanion. Then the intramolecular interactions in the transition state would occur by the inductive mechanism with the intensity no less than that of conjugation. Actually solvation with water molecules exerts a significant effect during the whole reaction event, and the strong covalent interaction by the mechanism of hydrogen bonding between strong nucleophilic centers of the reacting CH acid (such as NO_2 or COMe fragments) and solvent molecules causes a situation when the electronic effects change their nature, as can be traced by correlations of $\log k_D$ with various types of σ constants. Generally speaking, in this case a set of $\sigma\rho$ correlations of $\log k_D$ with different σ constants can exist, depending on the charge localized on the transition state fragment susceptible to interaction with the solvent. The occurrence of interaction of the carbanionic transition state with a solvent, making the structure planar, is confirmed by close correspondence between correlations XII and XI for $\log k_D$ and pK_a. Although the nature of the resonance effect remains unchanged in going from the kinetic series to the equilibrium series, the sensitivity constants ρ^- in the kinetic series are appreciably lower. Thus, to understand deviations from the correlation of $\log k_D$ with pK_a, it is necessary to compare the specific solvation states of a substituted methyl carbanion in the transition state and the same carbanion in the final (equilibrium) state. As already noted, an important feature of solvation of the transition state in a hydroxyl-containing solvent is certain contribution of covalent bonding with the solvent. Turning back to consideration of the effect exerted by DMSO as solvent on equilibrium carbanions, it should be reminded that in an orthodox theory this effect is presumed to be purely electrostatic [47]. At the same time, the results of the recent X-ray diffraction study [48] showed that the surrounding DMSO molecules also interact with atoms in carbanions bearing high electron density by the mechanism of hydrogen bonding with the DMSO methyl groups. The contribution of the H bonding to the total interaction energy can be significant. We believe that it is possible to "subtract" the contribution of electrostatic solvation from pK_a, preserving the contribution of H bonding, and thus to restore the uniformity of interactions in the pK_a and $\log k_D$ series [3]. Elimination of the electrostatic constituent from the experimental pK_a value of substituted methanes allowed us to linearize the relationship between the rate and equilibrium constants determined, respectively, in water and DMSO [3].

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