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Nontraditional Interpretation of Deviations from the Brønsted Relationship: Effect of Structural and Solvation Factors on the Equilibrium and Kinetic Characteristics of the CH Acidity in Polar Basic Nonaqueous Media

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Abstract—A concept is suggested for explaining deviations of certain CH acids from the linear Brønsted relationship. The major attention is given to ion–dipole interaction between the molecules of a polar aprotic solvent and dissolved carbanions. The concept is based on correcting the experimental pK_a values by eliminating the contributions from electrostatic solvation using data on the ionization constants of CH acids in the gas phase (ΔH^g). By the examples of acid dissociation of methyl CH bonds under conditions of established equilibrium in DMSO and kinetic data for deuterium exchange in a solution of an alkali metal amide in liquid ammonia, it was shown that for a series of compounds PhM$(CH_3)_{n-1}$ and M$(CH_3)_n$ (M = N, O, P, S, CO), and also for some other methyl derivatives all kinds of deviations from the Brønsted relationship are realized (those originating from specific conditions of stabilization of the transition state in the course of reaction; those due to electrostatic solvation of the equilibrium carbanions; and the deviations resulting from combined effect of the kinetic and equilibrium factors). Also, the Brønsted relationships were obtained for ionization of CH acid series covering compounds with aliphatic, quasiaromatic, and aromatic CH bonds (the deuterium exchange was performed in liquid ammonia without a catalyst). The Brønsted coefficient α 0.65 in this relationship suggests a higher degree of deprotonation of the CH bond in the transition state as compared to the catalytic exchange (α 0.3). The revealed difference is due to the different effect of electronic factors: In the catalytic deuterium exchange, the major contribution to the activation free energy ($\log k_D$) is made by the resonance effects of substituents, whereas in the noncatalytic deuterium exchange the inductive effect prevails.

Quantitative description of the reactivity of compounds in protolytic reactions is the subject of numerous studies. One of the main aspects of the problem is physical interpretation of the Brønsted relationship (1) correlating the reaction rate with the parameters controlling the acidity in solutions, and in particular elucidation of the causes of frequently observed deviations from (1).

$$\log k = \alpha \mathrm{p}K_a + C. \quad (1)$$

Here, k is the rate constant of a protolytic reaction; pK_a is the acidity parameter usually operative within a group of compounds belonging to the same reaction series; and α and C are constants within a reaction series.

Apparently, in the general case deviations from the linear Brønsted relationship (1) can be due to both kinetic ($\log k$) and thermodynamic (pK_a) factors. At the same time, various interpretations of this relationship suggested by now are based on the effect of kinetic factors, despite the fact that the results of such interpretations can give little information without additional consideration of the factors responsible for irregular variation of pK_a within the reaction series.

One of the goals of this study was revealing the role of the thermodynamic, factor using an approach that, in combination with the previously developed method for estimating the energy of electrostatic solvation of carbanions [1–4], allows convenient classification of the reactions under consideration depending on the causes of the observed deviations from the Brønsted relationship. Such a classification should facilitate successful analysis of the experimental results and promote wider use of the Brønsted relationship for predicting the rates of protolytic reactions from the experimental pK_a data.

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The approach suggested in this work has no claim on being universal, as it is based on the key principle that the prevailing type of interactions in solution in which pK_a was measured is the equilibrium electrostatic solvation of deprotonated charged species of the CH acids. Correspondingly, our approach can be applicable to any kinetic reaction series, but, as for thermodynamic series, its applicability is limited to the series involving solutions of CH acids and the conjugate bases (carbanions) in aprotic polar solvents with a low intrinsic acidity. The most promising medium in this respect is a solution of potassium or sodium dimsyl in dimethyl sulfoxide (DMSO). The advantages of this system are very weak capability for hydrogen bonding with various hydrogen donors and acceptors, high polarity of the reaction medium, high proton-acceptor power allowing evaluation of the acidity of very weak CH acids, etc. Furthermore, for DMSO the largest body of data is available on the ionization of various CH acids in it as a solvent. As for dissolved CH acids and their carbanions, as a rule, they have a polar center susceptible to the electrostatic effect of the solvent.

In this paper we present the principles of the developed approach and report on its testing as applied to reaction series with widely varied acidities of methyl and aromatic CH bonds, as influenced by substituents.

In parallel, by combining our approach to interpretation of deviations from the Brønsted relationship, extrathermodynamic relationships of the Hammett type, and analysis of the solvent effect on the CH acidity, we evaluated the effect of internal and external factors on the protolytic reactivity of compounds differing in the proton lability of CH bonds.

Because our approach actually supplements the concepts developed previously, it is appropriate first to briefly discuss some of the existing interpretations of the Brønsted relationships, choosing the most adequate interpretations. First, it should be emphasized that, on the whole, the existing concepts explain only particular aspects of protolytic transformations but not the whole pattern. Three lines in the existing interpretations can be distinguished. In studies classed with the first line, interpretation of the $\log k$–pK_a relationships is associated with the specific features of the event of proton transfer from a CH acid to a base. Within the framework of this approach, one of the most formalized models for analysis of the origin of the Brønsted relationships was developed [5]. It is based on the multiphonon process theory developed in the 1950–1960s for describing optical and radiationless transitions in one center. A doubtless success of this model was revealing a direct correlation between the variation of the Brønsted coefficient α and parameters depending on changes in the solvation shell of the reactants, redistribution of the electron density, and rearrangement of the molecular geometry. In particular, the model, in agreement with the experiment, predicts that the curvature of the Brønsted plot depends on the sum of the energies of the solvent reorganization and structural rearrangement of the reactants. Unfortunately, the mathematics of Dogonadze–Kuznetsov's model are sophisticated, which limits its practical use. A closely related approach is based on the principle of imperfect synchronization of protolytic reactions (see, e.g., [6, 7]). According to this principle, factors enhancing the stability of the reaction products (resonance, polar, and solvation effects) decrease the reaction rate relative to the rate of the Brønsted relationship if these factors operate after the reaction passes the transition state and increase the reaction rate otherwise. This theoretical approach allows prediction of the effect of the above factors on the kinetics of a protolytic reaction and gives insight into the origin of the curvature of the Brønsted plot. On the whole, studies classed with the first line, in accordance with their main principles, are limited to consideration of the elementary event of proton transfer, whereas the possible effect of the step mechanism of protolytic reactions on the applicability of the Brønsted relationship is not discussed at all.

Studies of the second group form, to a large extent, a separate field, because in these studies deviations from the linear Brønsted relationships are attributed to possible changes in the reaction mechanism. More precisely, it is always possible that, as the structure of a CH acid or base is varied, the linear relationship between $\log k$ and pK_a can be broken owing to transition from the mechanism in which the limiting stage is ionization of the CH bond (at which $\log k \sim$ pK_a) to the mechanism in which the reaction rate is determined not by ionization of the CH bond but by the subsequent stage characterized by different sensitivity to the reactant structure [8]. In this connection, it should be noted that in this paper we discuss the simplest protolytic reaction, hydrogen isotope exchange. This reaction is usually considered as a two-stage process. In the first stage, sensitive to hydrogen isotope substitution (k_1), a base detaches proton from a CH acid to form a carbanion, which is neutralized in the second stage (k_2). Each of the two consecutive stages of deuterium exchange can be limiting depending on the structure of the CH acid and protophilic properties of the medium. If the rate is limited by the second stage (k_2), then the Brønsted relationship is not fulfilled at all, because for different compounds of a reaction series any differences in the rate of the elementary second stage are possible. In the intermediate case, when within a reaction series the mechanism gradually changes in going from one compound to another as a result of growing contribution of the second stage to the overall deuterium exchange rate, the Brønsted plot becomes curvilinear (effect of internal return). Thus, to elucidate whether the nonlinearity of the Brønsted plot is indeed due to the change in the limiting stage of the process, it is necessary to thoroughly analyze the correlation of the structure of CH acids with the reaction kinetics and mechanism, values of the kinetic isotope effects, experimentally determined variations of the Brønsted coefficient α, etc.

Studies of the third group are aimed at revealing the role of the thermodynamic factor in deviations from the linear Brønsted relationship. The necessity to take into account the thermodynamic factor of ion association, preventing experimental observation of the linear correlation between $\log k$ and pK_a (or between $\log k$ and the acidity function H^-), was emphasized in many papers concerning behavior of CH acids in concentrated aqueous solutions of alkalis [8, 9]. On the whole, the thermodynamic factor as one of the causes of deviations from the Brøensted relationship is apparently underestimated in the literature.

It should be noted in conclusion that, to obtain a physically clear interpretation of the nonlinearity of the Brønsted relationship, it is necessary to develop, along with rigorous approaches (first group of studies according to our classification), also qualitative, maximally simple approaches, which can supplement each other and give a more complete and descriptive pattern.

Modification of the Brønsted relationship. Choice of appropriate reaction media. The integrating idea of our approach is combined study of the effect of structural and solvation factors on the strength of the CH acids in the gas phase (ΔH^g) and in solutions (pK_a, $\log K_D$). Pratical realization of this approach starts from considering in a series of similar compounds variation of pK_a in relation to the ionization constants in the gas phase (ΔH^g). A new point in this case is the use as a basis of the previously found linear correlation between gas-phase acid ionization constants (ΔH^g) and pK_a values in a series of very weakly solvated hydrocarbons, for which deviations toward lower pK_a (ΔpK_a) are due to the manifestation of the energetically favorable electrostatic effect of solvation of the conjugate carbanions [1–4]. The ΔH^g values, along with the pK_a values of reference hydrocarbons in the system potassium dimsyl–DMSO, cover a wide range of acidity. The strongest CH acidity is exhibited by fluoradene (**I**, ΔH^g 1397 kJ mol^{-1}, pK_a 10.5), and the lowest, by toluene (**II**, ΔH^g 1600 kJ mol^{-1}, pK_a 41); fluorene (**III**, ΔH^g 1483 kJ mol^{-1}, pK_a 22.9), diphenylmethane (**IV**, ΔH^g 1527 kJ mol^{-1}, pK_a 32.1), and cycloheptatriene (**V**, ΔH^g 1570 kJ mol^{-1}, pK_a 35.1) [1] exhibit intermediate characteristics. Deviations of the points from the straight line plotted for a reference hydrocarbon series are specific for each compound and can be considered as an approximate characteristic of the energy of electrostatic solvation of the carbanions.

To make certain that deviations from the basis line $\Delta H^g = f(pK_a)$ are indeed the criterion of electrostatic solvation of the carbanions, the values of $\Delta\Delta G_s = 2.3RT\Delta pK_a$ (where ΔG_s is the standard free energy of deprotonation in solution), obtained by the above-described simplest procedure, were compared to the $\Delta\Delta G_s$ values calculated within the modified reactive field model using a precision *ab initio* method for systems of the type DMSO–CH_3X–CH_2X^-, where X = SOMe, CN, COMe, NO_2.

The efficiency of the suggested procedure is illustrated by the fact that the obtained $\Delta\Delta G_s$ values correctly reproduce the order of the $\Delta\Delta G_s$ values calculated *ab initio* (deviations do not exceed 15 kJ mol^{-1} [10, 11]).

Of course, deviations from the basis correlation ΔH^g–pK_a correspond to the conditions of the established equilibrium and therefore cannot give full insight into the causes of deviations from the Brønsted plot, but they provide a basis for eliminating the thermodynamic factor from the causes of such deviations.

The next procedure in our approach is passing from the experimental pK_a values to the quantities $pK_a^{corr} = pK_a + \Delta pK_a$, free of the contribution from electrostatic interactions. The Brønsted relationship can thus be modified so that the quantities pK_a^{corr} would correspond to a hypothetical situation in which they characterize metal interchange under conditions when only the dispersion solvation is manifested throughout the reaction series. To conclude, the developed approach allows us to simply distinguish what factor (thermodynamic associated with electrostatic interactions in solution or kinetic) is mostly responsible for deviation of one or another compound from the linear Brønsted relationship.

Then, a problem arises of choosing reaction series (liquid-phase thermodynamic and kinetic) for a wide systematic study, based on the above-presented approach, of factors responsible for the limited applicability of the Brønsted relationship.

Taking into account one of the main postulates of the modern theoretical concepts, according to which the curvature of the Brønsted plot, generally speaking, continuously varies with varying structure of CH acids, it should be expected that the curvature of the resultant plot of $\log k$ vs. pK_a should be the most pronounced in the series of CH acids covering the maximally wide range of pK_a and $\log k$ values. The easiest way to assess the efficiency of our approach is to use published sets of the ΔH^g and pK_a values, on the one hand, and of the $\log k$ and pK_a values, on the other hand. Unfortunately, in the overwhelming majority of cases the Brønsted relationships could be constructed only for a relatively narrow range of pK_a values (8–10 pK_a units). Furthermore, the published sets of ΔH^g–pK_a and pK_a–$\log k$ data do not afford a common set (ΔH^+, pK_a, $\log k$) suitable for constructing reaction series in a wide range. Finally, it should be noted that the experimental data on $\log k_D$ accumulated by now are mainly suited for constructing the Brønsted dependences only for medium-strength CH acids ($10 < pK_a < 25$). In this connection, it is interesting to extend the range of pK_a values in which the Brønsted relationship is studied toward weaker CH acids, preferably compounds that would be weaker CH acids than the solvent. In this case, in order to make possible the correlation of the experimental data on kinetic reaction series including the same compounds as the thermodynamic series with the results of measuring pK_a and ΔH^g over the whole required range of their variation, it is necessary to know $\log k$ for very weak CH acids ($25 < pK_a < 50$). Examination of the problem showed that among diverse protolytic reactions the widest range of $\log k_D$ values compatible with the pK_a scale is covered by deuterium exchange reactions between various CH acids and various bases. In most cases, the kinetics of deuterium exchange were studied with a series of CH acids with varied substituents and a fixed base under identical reaction conditions. Since usually the sensitivity of a reaction center to electronic effects of substituents considerably increases with decreasing distance between the substituent and reaction center, it is prefereble to study hydrogen isotope exchange with CH acids in which the varied substituent is directly linked to the reaction center.

The above facts stimulated us to perform a kinetic study with three classes of structurally related CH acids characterized by known ΔH^g and pK_a. (1) Compounds containing substituents $M(C_6H_5)_{n-1}$ and $M(CH_3)_{n-1}$ (where M = N, O, P, S) in the α position relative to the same reaction center, methyl group (Table 1). Substituents $M(C_6H_5)_{n-1}$, being π donors, differ considerably in the electron-donor power. (2) CH acids in which the substituents at the methyl group are phenyl, benzoyl, 2-pyridyl, and 3-pyridyl. These substituents are typical acceptors. (3) Benzene and fluorobenzene; in the latter, the *o*-CH group is the most active in isotope exchange. The thermodynamic reaction series including these compounds are unique in that, depending on the substituent, their pK_a varies in the range $25 < pK_a < 50$, and the corresponding ΔH^g values, in the 100 kJ mol^{-1} range. To ensure measurable isotope exchange of the chosen weak CH acids, they should be treated with a very strong base. Therefore, as reaction medium for studying the effect of the structure of the selected CH acids on the rate of hydrogen isotope exchange we chose potassium (or sodium) amide in liquid ammonia. This medium exhibits a high protolytic activity. Furthermore, its capability for solvation of carbanions is very weak, which simplifies analysis of this factor on the acid–base interactions.

Hydrogen isotope exchange in the methyl group at the α position to substituents with a solution of an alkali metal amide in liquid ammonia. Strictly speaking, correlation of the pK_a data with the ΔH^g and $\log k_D$ values should be performed using data on the metal interchange equilibrium of CH acids in DMSO. However, at present the available experimental data on pK_a of very weak CH acids are insufficient. Obtaining reliable pK_a values is complicated by the fact that these quantities cannot be directly measured in DMSO, because the negative logarithm of the autoprotolysis constant of DMSO is 35.1, and this value restricts the range of acidities measurable in DMSO. Therefore, we were forced to use the results of indirect determination of pK_a in DMSO for compounds **X**, **XI**, and **XIV**, performed by the extrapolation procedure developed by Bordwell and Taft [23]. Furthermore, with the aim of a more complete description of the protolytic reactivity, we were forced to combine data on pK_a in the strongly polar DMSO (ε 46.6) with data on pK_a in weakly polar THF (ε 7.6). In contrast to DMSO in which alkali metal derivatives of the CH acids under consideration are, as a rule, dissociated to free ions, in THF the carbanions form various ion pairs with the counterions. Therefore, pK_a measurements in the weakly polar THF can give erroneous views on the absolute values of pK_a as measure of the equilibrium CH acidity. It was shown, however, that changes in the state of the alkali metal derivatives on replacement of DMSO by THF do not affect the pK_a values if these values in THF are calculated using the indicator scale established in DMSO relative to fluorene, for which pK_a 22.9 [15, 24]. This means that the solvent properties affect the basicities of the test and reference carbanions similarly. It was shown that for a very large set of organic and inorganic acids (~1000) the relative acidity does not change noticeably in

Table 1. Deprotonation energy of compounds containing varied substituent at the methyl group, and also of benzene and fluorobenzene in the gas phase (ΔH^g), pK_a values, rate constant of deuterium exchange in KNH_2–NH_3(l.) solution (k_D), factors of the partial deuterium exchange rate (log *f*), and resonance constants of substituents (σ_R^0)

Comp. no.	Compound	ΔH^g, kJ mol^{-1}	pK_a	*t*, °C	C_{KNH_2}, M	$k_D \times 10^5$, s^{-1}	log *f*	σ_R^0 [12]
VI	Acetophenone	1518 [13]	24.7 (DMSO)	–45	0.02[a]	210	4.1	0.19
VII	2-Methylpyridine	1579 [14]	34 (THF) [15,16]	–45	0.02[a]	0.05	0.7	–
VIII	3-Methylpyridine	1583 [14]	37.7 (THF) [16]	–45	0.02[a]	2.6	2.4	–
IX	Thioanisole	1591 [13]	38.6 (THF) [17]	–60	0.02	200 [18]	6.0	–0.19
X	Toluene	1600 [14]	41 (DMSO)	–45	0.02[a]	0.5	1.7	–0.10
				0	0.02	50		
XI	Dimethyl sulfide	1645 [13]	45 (DMSO)	0	0.45	30	0.48	–0.25
XII	Phenyldimethylphosphine [19]	–	–	0	0.02	110	1.9	–0.08 [20]
XIII	Anisole [21]	–	49 (DMSO)	25	0.06	4	–1.7	–0.36
XIV	Dimethyl ether	1709 [13]	(55)[b] (DMSO)	25	0.6	0.4	–2.6	–0.43
				50		2.2		
XV	*N*,*N*-Dimethylaniline [21]	–	–	25	0.06	0.09	–2.3	–0.48
XVI	Trimethylamine	–	–	65	0.6	0.27	(–4.1)	–0.53
						1.4		
XVII	Benzene	1680 [13]	47 [22][c]	–45	0.01	0.01	0	0
			(44.8) (THF)	0	0.02	0.7		
				0	0.05	1.1 [22]		
				25	0.05	11 [23]		
XVIII	Fluorobenzene-2D_1	1625 [13]	41.8 (DMSO)	–33	0.6	40000	6 [8]	

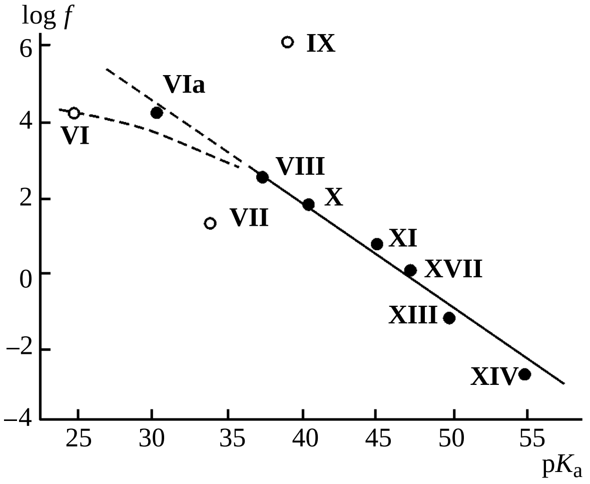
[a] Deuterium exchange was performed in the presence of sodium amide as catalyst. [b] Estimated by Eq. (2) using the value of ΔH^g given in the table. [c] Obtained by extrapolation of data on variation of pK_a(THF) in the series of polyfluoro- and polychlorobenzenes.

going from THF to DMSO. As the relative acidity scales are similar, pK_a measurements in THF make it possible to follow the deacidifying effect of electron-donor substituents up to pK_a(THF) ~50. The same is largely true for the pK_a values obtained in the other weakly polar solvents used in this work (dimethoxyethane, cyclohexylamine).

Deuterium exchange in the methyl group of **VI**–**VIII** and **X** is very fast; therefore, experiments were performed at very low temperature (–45°C) in the presence of poorly soluble sodium amide. With less acidic compounds **XIII** and **XIV**, for which the dedeuteration constants were determined in [21, 22], it was feasible to study the reaction kinetics in a more protophilic medium (C_{KNH_2} 0.06 M) and at room temperature. Finally, methyl CH acids **XIV** and **XVI** show a low activity in isotope exchange; with these compounds, deuterium exchange could be performed only at a high concentration of amide ions (C_{KNH_2} ~0.6 M) and at elevated temperatures. The experimental conditions and constants of deuterium isotope exchange calculated by the first-order kinetic equation (k_D) are listed in Table 1. Also given are the factors of the partial deuterium exchange rate, expressed relative to the rate constant of deuterium exchange k_D in benzene with the same solvent and at the same temperature and amide ion concentration. Note that, with hydrogen isotope exchange in benzene chosen as the reference reaction, it is possible to compare the relative acidities $f = k_D(C_6H_5X)/k_D(C_6H_6)$, which are independent, to a first approximation, of the catalyst concentration and temperature (X is a substituent in the ring or a heteroatom).

As seen from the figure, the plot of log *f* vs. pK_a(DMSO), constructed using data in Table 1, is a broken line with a break at pK_a ~38. The linear section covers the range of very weak CH acids **VIII**–**XI**, **XIII**, **XIV**, and **XVII**, whose pK_a ranges from 38 to 50. Compounds **VI**, **VII**, and **XVIII**, which are stronger CH acids (25 < pK_a < 38), show deviation from the linearity, which suggests that certain factors hinder the deuterium exchange in these compounds; these factors are yet to be revealed.

To interpret, in terms of our approach, the origin



Correlation between the factors of the partial rate of hydrogen exchange in some very weak CH acids in the catalytic system NH_2^-–NH_3(l.) and the pK_a values. The Roman figures correspond to the compound numbering in the text. Compounds denoted by black circles obey the Brønsted relationship, and those denoted by light circles deviate from it. The point for **VIa** corresponds to the corrected value, pK_a^{corr} 30 (acetophenone).

of deviations from the linear plot in Fig. 1, we replaced the pK_a values obtained by direct equilibrium measurements by the pK_a values corrected taking into account the electrostatic solvation of carbanions with solvent molecules. For this purpose, available data on ΔH^g and pK_a of CH acids **VIII**–**XI**, in total with similar data for reference hydrocarbons **I**–**V**, were fitted by the linear relationship

$$\Delta H_{as} = (7.4 \pm 0.6)pK_a + (1308 \pm 10);\ r\ 0.982,\ s\ 9,\ n\ 10. \quad (2)$$

The points for 2-methylpyridine (**VII**, pK_a 34) and acetophenone (**VI**, pK_a 24.7), deviating from the linear plot, were not included in (2). Correlation (2) was used as a basis for estimating the corrected values of pK_a^{corr} = pK_a + ΔpK_a, where ΔpK_a is the shift of the points deviating from correlation (2) toward lower pK_a (see figure). As a result, we obtained pK_a^{corr} 30 for acetophenone (**VI**) and pK_a^{corr} 37 for 2-methylpyridine (**VII**). In the case of the other compounds in hand, pK_a^{corr} = pK_a. Only the data for acetophenone obey the modified Brønsted relationship, which can be obtained for the series **VI, VIII, X, XI, XIII**, and **XVII** using for acetophenone pK_a^{corr} 30 instead of pK_a. The corresponding relationship is as follows:

$$\log f_D = -(0.32 \pm 0.04)pK_a^{corr} + (14.4 \pm 1.8); \quad (3)$$

$$r\ 0.975,\ s\ 0.47,\ n\ 6.$$

It can be readily seen that the length of the linear section of the curve in the figure increases as a result of the above procedure, and the linearity range of pK_a^{corr} reaches 19 units. However, for thioanisole (**IX**) and fluorobenzene (**XVIII**) deviations from (3) are still large, despite the fact that in the thermodynamic reaction series [Eq. (2)] these compounds show no deviations from the linear correlation of ΔH^g with pK_a. Finally, for 2-methylpyridine in going from pK_a to pK_a^{corr} the deviation from linear relationship (3) decreases but remains significant (ΔpK_a 5.2).

We can present some comments concerning the electronic and solvation factors responsible for the linearity of the modified Brønsted relationship (3) and for deviations from this relationship.

Compounds **VIII, X, XI**, and **XVII**, for which variation of the CH acidity obeys both the linear Brønsted relationship (3) and the thermodynamic correlation (2) between ΔH^g and pK_a, form a common reaction series with the same internal activation barrier and the lack of specific effect from changes in the solvation shell around the reacting CH acids [25].

From the preceding text, it is seen that deviation from the linearity for acetophenone (see figure) has a thermodynamic origin. This can be interpreted using Pearson's concept of hard and soft acids and bases [26]. Namely, the enolate anion of acetophenone in which excess negative charge is localized on the oxygen atom (hard nucleophilic center) forms in DMSO solutions stronger solvation complexes than ions of alkali metal hydrocarbon salts fully separated by the solvent.

As already noted, thioanisole (**IX**) is peculiar in this respect in that it is characterized by increased rate of deuterium exchange (log *f*) relative to the Brønsted straight line (3), and this fact has a kinetic origin. Published data show that the different behavior of thioanisole in the series of the kinetic and thermodynamic CH acidity is due to different manifestation of the structural features of the carbanion transition state and the stable form of the thioanisole carbanion after completion of metal interchange. Indeed, in the stable planar carbanion (similar to the nondissociated thioanisole molecule), despite π conjugation of the lone electron pair of the methylthio group or SCH_2^- fragment with the phenyl ring, the integral redistribution of the electron density is insignificant, because the lone electron pair interacts primarily with the filled π leveles of the ring, forming occupied bonding and antibonding combinations. Such interaction does not result in extra stabilization of the thioanisole carbanion [27, 28]. On the contrary, participation of the phenyl ring in the electron density distribution in the carbanion transition state is insignificant and mainly has the inductive nature, which is due to the loss of coplanarity of the system. In other words, in this case the phenyl group acts mainly as σ acceptor (σ_I 0.1) favoring a different kind of conjugation: conjugation of the vacant orbitals of the sulfur atom with the lone electron pair of the negatively charged carbon atom. This results in extra stabilization of the carbanion transition state and hence in an abnormally high rate of deuterium exchange in the methylthio group.

The significant effect of the dynamic solvation factor on the rate of proton transfer from the fluorobenzene-2D (**XVIII**) molecule to amide ion is apparently responsible for the fact that this compound obeys the thermodynamic relationship (2) but strongly deviates from the Brønsted relationship (3). This problem was discussed in detail in [6, 7]. Here we will only note that our interpretation is based on the assumption that in this case rearrangement of the solvent around the reacting system, initiating a protolytic reaction, occurs faster than the system reaches the transition state. Such a nonequilibrium character of solvation, in accordance with the imperfect synchronization principle, should result in the higher rate as compared to that predicted by the Brønsted relationship.

As compared to anomalies observed with other CH acids, the fact that for 2-methylpyridine (**VII**) variations of $\log f$ and $\mathrm{p}K_\mathrm{a}$ cannot be described by the modified Brønsted relationship (3) and the thermodynamic relationship (2) between ΔH^g and $\mathrm{p}K_\mathrm{a}$ is also broken is more difficult to understand. One of the possible explanations is that under conditions of protolytic equilibrium a solution of 2-methylpyridine in THF contains electrostatically solvated carbanions, which should result in lower $\mathrm{p}K_\mathrm{a}$ compared to $\mathrm{p}K_\mathrm{a}^\mathrm{corr}$ for free 2-methylpyridyl carbanions. At the same time, the effect of liquid ammonia as solvent on the rate of hydrogen exchange in compound **VII** in which the methyl hydrogen atom shows increased lability is manifested in reaction deceleration due to delayed rearrangement of the solvation shell around the reaction center.

Another possible cause of the break of the modified Brønsted relationship (3) with 2-methylpyridine can be steric destabilization. Namely, in a solution of an alkali metal amide in liquid ammonia the dipolar repulsion between the CH_2^- group and the lone electron pair of the adjacent nitrogen atom abnormally decreases the "internal" acidity. A similar but weaker interaction is probably preserved in the initial nondissociated CH acid **VII**, as indicated by the results of *ab initio* quantum-chemical study of the effect of the adjacent lone electron pair of nitrogen on the C–H bond in the methyl group of 2-methylpyridine [29].

Thus, the above discussion shows that deuterium exchange in a solution of potassium (or sodium) amide in liquid ammonia is a convenient object for studying the protolytic reactivity, because the fulfillment of the Brønsted relationship (3) after certain modifications and the deviations from this relationship give insight into effects determined by the structure of CH acids.

Of particular significance for elucidating the reaction mechanism is the use of the coefficient α in (3) for studying the structure of the transition state. Usually, α ranges from 0 to 1 depending on the type of the series, namely, on the reactants and reaction medium. The numerical value of α is interpreted as the extent of the structural and electronic similarity of the transition state with the initial CH acid (for low α) or the stable carbanion (for high α) [25]. For the reaction under consideration, $\alpha = 0.3$, which suggests that the transition state is located on the reaction coordinate closer to the initial CH acid and farther from the ion pair carbanion–metal ion, as compared, e.g., to deprotonation of the CH bond in substituted benzenes (where $\alpha = 1$). A similar result, $\alpha = 0.37$, was obtained in [30] from the dependence of $\log k_\mathrm{D}$ on $\mathrm{p}K_\mathrm{a}$ for a series of fluorenyl compounds. Streitwieser *et al.* [30] concluded from this fact that in the transition state of deuterium exchange the degree of charge delocalization is only 37% of that observed in the corresponding carbanions. The close values of α for the reaction series under comparison allow us to conclude, without considering the different chemical nature of these systems, that in the compounds with the reactive methyl group examined in this work the hybridization of the carbon atom at deprotonation also changes from the initial sp^3 state to the transition state in which the *s* character of the hybridized orbital is more pronounced by 30%. This means that the transition state has a pyramidal structure.

The results of using Brønsted relationship (3) form only a part of the quantitative basis for discussing the mechanism of electronic interactions in reacting systems. The Brønsted relationship by itself does not reflect quantitatively various electronic effects of substituents on the reaction rate. However, these effects are reflected by another particular form of the linear free energy relationship: Hammett equation. To obtain a pattern of electronic effects of substituents at the sp^3 carbon atom in the methyl group, we extended the range of compounds under consideration and included phenyldimethylphosphine (**XII**), dimethyl ether (**XIV**), and trimethylamine (**XVI**). For these compounds, published data on pK_a to be correlated with ΔH^g and $\log f$ are lacking, but data on $\log f$ and on σ constants are available. Attempts to correlate the experimental $\log f$ values with various types of σ constants showed that only with the resonance constants σ_R^0 the correlation coefficient is high:

$$\log f = (11.2 \pm 0.9)\sigma_R^0 + (2.6 \pm 0.3);\ r\ 0.986,\ s\ 0.42,\ n\ 8. \quad (4)$$

As judged from the trends in σ_R^0, the kinetic CH acidity increases with decreasing donor power of substituents.

As expected, deviations from relationship (4) are observed for 2-methylpyridine **VII** and thioanisole **IX** in which a significant contribution to $\log f$ is made by the anomalous electronic effects considered above. Data for these compounds were excluded from the $\sigma\rho$ analysis.

Correlation (4) is interesting from the viewpoint of increasing the number of studied reaction series in which variations of the correlated quantities are characterized exclusively by the σ_R^0 constants, and also of revealing common features in the nature of resonance effects of different types. In particular, it follows from the literature that the relationships similar to that describing the effect of substituents on the kinetic CH acidity of the compounds under consideration (4) are also applicable to studying conjugation in neutral molecules and carbocations in which the reaction center and substituents are directly adjacent to each other. In this context, we should primarily mention the paper by Mariott and Topsom [31] who described by the σ_R^0 constants the effect of substituents X on the HOMO energy in compounds $XC{\equiv}CH$ and $XCH{=}CH_2$. In these compounds, the electron is mainly removed from the HOMO localized on the atom with the strongest donor power. It follows from this relationship that the conjugation in the molecular systems under consideration can be not only evaluated by the σ_R^0 constants, but also directly expressed as the electron density transferred between the substituent and reaction center. The validity of this conclusion is indirectly confirmed by the results of *ab initio* quantum-chemical calculations (at the STO–3G level) of the electron transfer (*q/e*) between substituent X and the rest of the carbocation in the species $XCH{=}CHCH_2^+$, $4\text{-}XC_6H_4CH_2^+$, and XCH_2^+ (X = NH_2, OH, F, Me, CF_3, CN, CHO, NO_2) [32].

Comparison of the trend in variation of the σ_R^0 constants, given by Eq. (4), with the published results of calculation of the electron density transferred from the anionic center CH_2^- to the fragment $(CH_3)_{n-1}M$ in the series of carbanions also shows that the resonance effect strongly depends on the transferred charge. If the M atom in the α-position relative to the anionic carbon atom was a lone electron pair, the resonance effect arises on mixing of the antibonding σ^* orbital formed by the M and C^- atoms with the *n* orbital of the lone electron pair of M (negative hyperconjugation [33]). On the contrary, if the first atom of the group linked to the anionic carbon atom is the carbon atom, the acidification of the methyl group in the CH acid molecule is due to the $2p_z\pi$ interaction described as $p\pi$-electron hyperconjugation.

Consider as example the nature of the electronic interactions determining the CH acidity of dimethyl ether (**XIV**) and dimethyl sulfide (**XI**). In this case, both M and C^- atoms are donors. According to calculations [34], the low acidity of the CH bond in the $(CH_3)_2O$ molecule is due to the fact that in the conjugate carbanion $CH_3OCH_2^-$ the electron-rich OCH_3 group does not noticeably take up the excess negative charge. The enhancement of the gas-phase and kinetic CH acidity in going from dimethyl ether to dimethyl sulfide is due to considerable weakening of the counterconjugation, with the electron density localized on the SMe group appearing to be noticeably higher than on the OMe group. The calculated charge distribution, together with data on shortening of the $S{-}CH_2^-$ bond and, to a lesser extent, pyramidal geometry of the CH_2^- group, is consistent with the description of carbanion stabilization by the negative hyperconjugation model [33].

The above discussion concerned revealing the role of the resonance effect in enhancement of the CH acidity of the compounds $(CH_3)_nM$ (M = O, S, N). It can be expected that the similar reaasoning is applicable to compounds $(CH_3)_{n-1}MC_6H_5$. It is significant in this context that data in Table 1 do not demonstrate existence of a common conjugation system in the anions $(C_6H_5)_{n-1}MCH_2^-$, favored by coplanar arrangement of the molecular fragments. Actually the heteroatom M fully isolates the anionic center (C^- atom) from the donor resonance effect of the phenyl ring (σ_R –0.1), and the phenyl ring exerts only the inductive effect (σ_I 0.1). The acidifying effect of the phenyl ring can be readily seen from the increase in $\log f$ on replacement of the methyl group by the phenyl rings in $(CH_3)_nM$ molecules (Table 1).

If the methyl group is directly linked to the phenyl ring (compound **X**) or is separated from it by a group containing no lone electron pair on the first atom (compounds **VI**–**VIII**), the interaction in the conjugated carbanions is still controlled by electron density transfer between separate fragments, depending, in turn, on the σ_R^0 constants. Among the considered class of compounds, the largest shift of electron density from the anionic carbon atom to the electron-acceptor group at the α position is observed in the simplest carbanion of acetaldehyde (~0.6 *e*) [35] and its phenylated analog **VI**. Correspondingly, the latter compound is characterized by the reversed sign of the resonance effect (σ_R^0 0.17).

Let us then discuss the sensitivity constant ρ_R^0 in relationship (4). It should be borne in mind that the sign and value of $\rho_R^0 = 11.2$ are associated with generation of an additional negative charge on the reaction center in the transition state as compared to the initial reactants. In our case, ρ_R^0 is large and positive, i.e., the structural possibilities of the transition state are manifested to a full extent owing to conjugation. A similar pattern of transfer of the resonance effect through a heteroatom was observed previously [36] in a system in which the reaction center (methyl group) is directly linked to the positively charged nitrogen atom, which is, in turn, incorporated into the aromatic ring. Kinetic sudy of the deuterium exchange of the N–CD_3 group in 3- and 4-substituted 1-methylpyridinium iodides with aqueous alkali showed that the substituent effect correlates with the σ_R^0 constants. However, in this reaction series ρ_R^0 is lower (6.5) than in (4); this is probably due to different charge distributions in the transition states of these reactions: Ionization of the CH bond in pyridinium iodides is accompanied by neutralization of the positive charge, whereas in the reaction series examined by us the negative charge of the methyl carbon atom sharply increases in the transition state of deuterium exchange.

Deuterium exchange in liquid ammonia in the absence of catalyst. Let us now discuss the following theoretically important question: How will variation of the proton-acceptor power of a base affect the structure of the transition state in hydrogen isotope exchange? To this end, it is approriate to supplement the kinetic data on catalytic isotope exchange in a solution of potassium amide in liquid ammonia by similar data on the exchange in straight liquid ammonia. The solvation effect in both reaction media should be similar, because the solvent is the same. At the same time, the catalytic activity of the amide ion considerably exceeds that of the ammonia molecule, which is a relatively weak proton acceptor: pK_a 9.1. To reveal common and specific features in the effect of both proton acceptors, we consider the effect of the protophilic properties of the medium on the Brønsted coefficient α. The kinetic data on the noncatalytic and catalytic hydrogen isotope exchange in the compounds considered in the preceding section cannot be compared because of the kinetic inertness of most of them in liquid ammonia (the reaction rates are too low to be measured). For these experiments, stronger CH acids should be chosen in which the heterolytic cleavage of the CH bond as a result of acid–base interaction is possible in the presence of a weaker base. In this context, we gave attention to the paper by Shatenshtein et al. [37] in which attempts to find a correlation between pK_a and $\log k_D$ in liquid ammonia without a catalyst were made with two series of compounds: (1) fluorene **III**, diphenylmethane **IV**, indene **XIX**, and triphenylmethane **XX**, i.e., hydrocarbons with a labile aliphatic CH bonds and large extent of delocalization of the negative charge in the carbanions; (2) isomeric *o*- (**XXI**), *m*- (**XXII**), and *p*-carboranes (**XXIII**), which are electron-deficient molecules with an unusual valence state of the carbon atom (the CH bonds in these compounds are pseudoaromatic). Ionization of the CH bond in carboranes yields carbanions with a large extent of delocalization of the electron density on the reaction center.

Although the linearity of the plot of $\log k_D$ vs. pK_a in [37] offered an independent confirmation of the correctness of the previous estimates of pK_a for isomeric carboranes, the use of a common Brønsted relationship for analysis of variation of $\log k_D$ and pK_a in so dissimilar series of compounds provokes questions. First of all, in [37] the deuterium exchange of aliphatic and quasiaromatic CH bonds can be described by a common Brønsted relationship, whereas other published data show that the Brønsted relationship is inapplicable to protolytic processes differing in the mechanism [8]. Furthermore, the kinetic data for each group of the CH acids differing in the character of stabilization of the reaction center in the course of deuterium exchange are few. Finally, the results of remote extrapolation of the experimentally measured rate constants of deuterium exchange in fluorene **III** and indene **XIX** cannot be considered as reliable. The kinetics of deuterium exchange in these compounds were studied at 0–25°C, whereas the Brønsted relationship was obtained for 120°C. The errors of the $\log k_D$ values were not reported, but they should be assumed to be relatively large.

To find whether the correlation in [37] is occasional or it indeed characterizes the elementary event of proton transfer, we extended the range of investigation objects by including acetophenone (**VI**), 2-methylpyridine (**VII**), 4-methylpyridine (**XXIV**), diphenyl thioformal $(C_6H_5S)_2CH_2$ (**XXV**), triphenyl orthotrithioformate $(C_6H_5S)_3CH$ (**XXVI**), and 2-methylbenzoxazole (**XXVII**), i.e., compounds with relatively low pK_a at which the noncatalytic exchange in liquid ammonia is feasible. Additionally, to examine the applicability of the correlation in [37] to the deuterium exchange of the aromatic CH bond, we studied the exchange kinetics of 1,3-difluorobenzene **XXVIII**. In

Table 2. pK_a values of selected CH acids, rate constants of their deuterium exchange (k_D) with liquid ammonia without catalyst, and inductive (σ_I) and resonance (σ_R^0) constants of complex fragments

Comp. no.	Compound	pK_a	t, °C	$k_D \times 10^5$, s^{-1}	–log k_D, 25°C	–log k_D, 120°C	σ_I	σ_R^0
III	Fluorene [37]	22.9 (DMSO)	25	16	3.8	–	–	–
IV	Diphenylmethane	32.1 (DMSO)	120	0.0007	–	8.2	0.06[a]	0.10 [12]
VI	Acetophenone	24.7 (DMSO)	0	1.0	–			
			15	2.4	–	2.8[b]	0.19	0.17
			25	5.8	4.24			
VII	2-Methylpyridine	34 (THF)	120	0.039	–	6.4	–	–
XIX	Indene [37]	20.1 (DMSO)	25	135	2.85	–	–	–
XX	Triphenylmethane	30.7 (DMSO)	120	0.02	–	–	–	–
XXI	*o*-Carborane [37]	23.3	60	56	–	(0.5)[b]	0.30 [38]	0.004 [38]
		(dimethoxyethane)	50	140				
			–30	500				
			25	6000	1.22			
XXII	*m*-Carborane [37]	27.9	25	0.3	5.52	–	0.21 [38]	–0.036 [38]
		(dimethoxyethane)	120	10	–	4.0		
XXIII	*p*-Carborane [37]	30	25	(0.04)[c]	(6.4)	–		
		(dimethoxyethane)	50	0.085				
			120	0.42	–	5.4	–	–
XXIV	4-Methylpyridine	32 [16] (THF)	120	0.018	–	6.7	–	–
XXV	Diphenyl thioformal $(C_6H_5S)_2CH_2$ [18]	30.8 [39] (cyclohexylamine)	120	0.6	–	5.2	0.18[a]	–
XXVI	Triphenyl orthotrithioformate $(C_6H_5S)_3CH$ [18]	22.8 [39] (cyclohexylamine)	120	20	–	3.7	0.22[a]	–
XXVII	2-Methylbenzoxazole	(28) (DMSO)	120	5.5	–	4.2	–	–
XXVIII	1,3-Difluorobenzene	34.3 [40] (THF)	120	0.0073	–	7.14	–	–

[a] The σ_I constants were determined by formulas (7) and (8), see text. [b] Extrapolation by the Arrhenius equation. [c] Extrapolation using data of [37].

its carbanion the negative charge arising on the cyclic carbon atom cannot efficiently interact with the π system. The results of our kinetic measurements, along with the values of log k_D and pK_a from [37], are listed in Table 2. Measurements were performed in liquid ammonia at 25 and 120°C; in some cases, the rate constants were recalculated to these temperatures using the Arrhenius parameters. To obviate a limitation originating from the large differences in the deuterium exchange rates for the compounds under consideration, we studied separately the low- and high-temperature Brønsted relationships. Attempts to correlate the log k_D and pK_a values for the minor fraction of compounds that are moderately strong CH acids (20 < pK_a < 30) result in large scatter of the points. Satisfactory correlation can be obtained only with pK_a^{corr} used instead of pK_a for acetophenone (**VI**) and indene (**XIX**, ΔH^g 1488 kJ mol^{-1}). For **XIX**, in contrast to fluorene, the experimental pK_a is by 6 lower than the hypothetical value (pK_a^{corr} 26) corresponding to Eq. (4), i.e., to the case when the carbanion of **XIX** is not subject to electrostatic solvation. The low-temperature correlation between the rate constants of deuterium exchange in liquid ammonia (25°C) and the equilibrium constants of metal interchange, corrected for electrostatic solvation, has the form

$$\log k_D = -0.74\mathrm{p}K_a^{corr} + 15.97;\ r\ 0.927,\ s\ 0.7,\ n\ 5. \qquad (5)$$

The point for fluorene (**III**) deviates from correlation (5). We have no reasonable explanation for this deviation. A similar high-temperature (120°C) linear correlation for weaker CH acids (25 < pK_a < 35)

$$\log k_D = -0.60\mathrm{p}K_a + 12.89;\ r\ 0.925,\ s\ 0.8,\ n\ 8. \ (6)$$

does not include outlying triphenylmethane (**XX**), triphenyl orthotrithioformate (**XXVI**), and 2-methylpyridine (**VII**).

The fact that the fragments $(C_6H_5)_3C$ and $(C_6H_5S)_3C$ accelerate the reaction to a lesser extent than expected by their experimental pK_a values is probably due to the steric effect: it is known that introduction of the increasing number of the C_6H_5 and C_6H_5S groups causes growing steric hindrance in the transition state of the reaction.

As for the causes of deviation from (6) of data for 2-methylpyridine (**VII**), the following should be noted. The above-discussed data show that deviations from linear relationship (2) and modified Brønsted relationship (3) can be due to two factors: (i) increased electrostatic effect of the solvent (DMSO) on the carbanion under conditions of established equilibrium (pK_a) in combination with slow solvation of the reacting systems in the course of deuterium exchange ($\log k_D$), or (ii) specific structural features of the 2-methylpyridyl carbanion, characterized by repulsion between the closely located lone electron pairs of the anionic carbon atom and cyclic nitrogen atom. The second explanation seems more probable in view of the fact that data for 4-methylpyridine (**XXIV**) in which there is no such repulsion do not deviate from the common Brønsted relationship (6) for deuterium exchange in liquid ammonia without catalyst, whereas data for 2-methylpyridine are outliers.

Existence of both correlations (5) and (6) shows that the varied structural factors affect similarly the kinetic and thermodynamic CH acidity of aliphatic and quasiaromatic CH acids. For aliphatic CH bonds this is quite natural, whereas for quasiaromatic CH bonds a different Brønsted plot could be expected, taking into account different, according to the generally accepted views, mechanisms of deuterium exchange of these CH bonds. The point is that in hydrogen isotope exchange in isomeric carboranes the D/T kinetic isotope effect was close to unity: $k_D/k_T \sim 1.1$ [37]. This fact gave Shatenshtein *et al.* [37] grounds to conclude that the transition state in this reaction is different from the common three-center model. At the same time, for deprotonation of an aliphatic CH bond (e.g., in indene or fluorene), k_D/k_{TM} is within 2.0–2.2 [37]. Such a value can be attained only if in the limiting stage of proton transfer from the CH acid to the ammonia molecule the structure of the three-center transition state is approximately symmetrical and the internal return has an insignificant effect on the exchange mechanism. We think that the viewpoint of Shatenshtein et al. is controversial. The fact that CH acids of two different groups form a common reaction series suggest gradual rather than jumpwise structural changes of the three-center transition state in the stage of proton transfer. In particular, in the limiting case, when the isotope effect is virtually lacking, the transition state can be considered as an extremely asymmetrical three-center system. After making sure that the linear relationships (5) and (6) between $\log k_D$ and pK_a are general for deuterium exchange of almost all the compounds under consideration in liquid ammonia without catalyst, let us compare the coefficient α in the Brønsted relationship (5) or (6) found for the noncatalytic deuterium exchange (α 0.65) with the estimate of the same coefficient (α 0.30) for deuterium exchange of methyl derivatives, catalyzed with amide ions [Eq. (3)]. Based on the fact that the coefficients α obtained are a measure of the relative stabilization by electronic effects of the transition state relative to the initial and final states, we assume that the increased α for noncatalytic deuterium exchange is consistent with the theoretical conclusions concerning the shift of the transition state along the reaction coordinate with changing strength of the catalyst. It is known that the theory predicts the shift of the transition state toward the carbanion and not toward the CH acid with decrease in the proton-acceptor power of the base, causing a decrease in α [25].

In the previous section, we have examined the dependence of the rate constants of deuterium exchange catalyzed with NH_2^- ions on the resonance σ_R^0 constants as applied to compounds whose molecules were conventionally divided into fragments. One of them, methyl group, was considered as a fixed reaction center, and the other, as a varied fragment (substituent). We restrict the correlation analysis of compounds exchanging in liquid ammonia without catalyst to a group of compounds of different classes: **IV**, **XX**–**XXIII**, **XXV**, and **XXVI**. In these molecules, the hydrogen atom of the CH bond being deprotonated acts as the reaction center, and the rest of the molecule (its core) is considered as an integral complex substituent. Attempts to use complex molecular fragments for simplified $\sigma\rho$ analysis requires certain comments. Firstly, the available set of resonance σ_R^0 constants of such fragments is not representative; it includes only **IV**, **XXI**, and **XXII** (Table 2). Nevertheless, even these data are sufficient to state that, in contrast to the reaction series of deuterium exchange in a solution of potassium amide in liquid ammonia, for noncatalytic deuterium exchange the σ_R^0 constants do not characterize the electronic effects in molecules (Table 2). Secondly, among the compounds of the considered series the inductive σ_I constants were determined experimentally only for the *o*- and *m*-carboranyl fragments (**XXI**, **XXII**). However, it is possible to take into account indirectly the inductive effect of the other complex fragments by summing up the contributions to σ_I, made by separate substituents forming the fragments. Indeed, a large body of data accumulated by now shows that the inductive effects in compounds $X^1X^2CH_2$ and $X^1X^2X^3CH$ are approximately additive, even for substituents X^1, X^2, and X^3 of different chemical nature. The inductive σ_I constants of the fragments containing two and three substituents were estimated by the additive scheme using the formulas obtained in [41] for di- and trisubstituted methyl groups:

$$\sigma_I(X^1X^2CH) = 0.297[\sigma_I(X^1) + \sigma_I(X^2)] + 0.005, \quad (7)$$

$$\sigma_I(X^1X^2X^3C) = 0.248[\sigma_I(X^1) + \sigma_I(X^2) + \sigma_I(X^3)] + 0.004. \quad (8)$$

In our case, $X^1 = X^2 = X^3 = C_6H_5$ or $X^1 = X^2$ $X^3 = SC_6H_5$.

The σ_I constants of the fragments, calculated by formulas (7) and (8) from $\sigma_I(C_6H_5)$ 0.1 and $\sigma_I(C_6H_5S)$ 0.3, are listed in Table 2. Based on data of Table 2, the correlation of $\log k_D$ of deuterium exchange of the aliphatic CH bond in compounds **IV, XXI, XXII**, **XXV**, and **XXVI**, containing complex fragments, with the inductive σ_I constants can be expressed as follows:

$$\log k_D = 30.3\sigma_I - 9.94; \; r\ 0.980, \; s\ 0.61, \; n\ 6. \quad (9)$$

Thus, in contrast to the above-discussed reaction series of the catalytic deuterium exchange, in which $\log k_D$ correlates with the resonance σ_R^0 constants, in the case under consideration the effect of complex molecular fragments on the reaction center is purely inductive. Because the molecular core is directly bonded to the hydrogen atom being removed, the inductive effect is manifested to a maximal extent (ρ_I ~30). A similar pattern is observed with deuterium exchange in deuterated *o*-substituted benzenes with a solution of potassium amide in liquid ammonia. In these compounds, the electron pair of the aromatic CH bond lies in the nodal plane of the π system, which excludes any conjugation. At the same time, the o-substituent is more remote from the reacting CH bond, and therefore the inductive effect is manifested to a lesser extent than in the above-discussed series (ρ_I ~11) [8]. *m*-Difluorobenzene **XXVIII**, in which the F substituents are separated from the reaction center of the aromatic CH bonds by two other bonds, shows a peculiar behavior in noncatalytic deuterium exchange with liquid ammonia. It seems that in this case the conjugation of the aromatic CH bond with the π system is significant. This is manifested in the fact that the combined effect of the donor F substituents sharply decreases the kinetic CH acidity, i.e., the resonance effect prevails over the inductive effect (Table 2).

EXPERIMENTAL

We used commercial chemicals with natural isotopic abundances, which were purified; their constants agreed with reference data. The purity of the initial compounds was checked by gas–liquid chromatography. As solvent we used ND_3 (99.5 at. % D) purchased from the Pilot Plant, *Prikladnaya Khimiya* Russian Scientific Center. Weighed portions of the initial substances were quickly dissolved in liquid ND_3 in the presence of alkali metal amide (all the tested compounds are soluble in ammonia even at –50°C). The g-atom ratios of the solvent to test compound ranged from 40 to 70. The reaction was stopped by adding excess anhydrous ammonium chloride to the strongly cooled solution. After evaporation of ammonia, the samples were extracted with diethyl ether and distilled. The position of deuterium in the molecules was checked by a decrease in the intensity of the absorption bands of aliphatic CH bonds (2900–3100 cm^{-1}) in the IR spectra. The deuterium concentration in the methyl group was determined by low-voltage mass spectrometry with an MI-1201 instrument. The procedure of kinetic experiments and equipment for working with liquid ammonia are described elsewhere [22, 42]. The experimental results were treated by the least-squares method. The rate constants calculated by first-order equations were stable in all the examined systems.

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