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The Hydrogen Bond and CH Acidity

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A systematic account is given of quantitative data on the properties of the hydrogen bonds formed by CH acids as proton donors and the influence of the nature of the substituents and of the steric and electronic structures of CH acids on the strength of these bonds is discussed. The studies in recent years devoted to the equilibrium and kinetic CH acidity are examined and the factors responsible for what is in many instances an "anomalous" behaviour of CH acids are analysed. The proton-donating capacity in hydrogen bonds and CH acidity are compared.
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I. INTRODUCTION

Protolytic reactions occupy one of the central positions in the chemistry of organic compounds. CH acids, grouped in a special class of compounds, have been arousing constant interest owing to the specific features of the factors determining their reactivity.[1,2] Hydrogen bonds involving CH acids[3] play an important role in protolytic reactions, since their properties influence the kinetics and mechanism of reactions involving proton transfer. The quantitative results of studies in this field are so far not numerous, but it is already clear that even relatively weak C–H...B hydrogen bonds can alter not only the energy profile of the process but also its probability characteristics, because the reactants involved in hydrogen-bonded complexes are close to one another and are oriented relative to the proton transfer reaction coordinate.

The question of the relation between the proton-donating capacity in C–H...B hydrogen bonds and thermodynamic and kinetic CH acidity arises naturally. For OH, SH, and NH acids, these relations have been studied on numerous examples.[4,5] On the other hand, in the case of CH acids, such comparisons have seldom been made. This review deals with the quantitative results of studies of hydrogen bonds and the acidity of CH groups polarised by electron-accepting substituents. The characteristics of the influence of the steric and electronic structures of CH acids on the strength of C–H...B hydrogen bonds are analysed. In conclusion, the proton-donating capacity of CH acids is compared with their kinetic and equilibrium acidities.

II. ASSOCIATION OF HALOGEN-SUBSTITUTED HYDROCARBONS

The CH groups polarised by electronegative halogen atoms form C–H...B hydrogen bonds with various bases. One of the first compounds for which such bonds had been observed spectroscopically was chloroform.[6] After the addition of bases, B, to chloroform, an increase of the width and intensity of the stretching vibration band is observed in its infrared spectrum, while for strong bases this band undergoes a bathochromic shift.[3] For example, in mixtures with triethylamine (TEA) the magnitude of this shift $\Delta\nu$(CH) reaches 80 cm^{-1}.[6]

Table 1. Thermodynamic characteristics of the association of $CHCl_3$ with various electron donors in cyclohexane and carbon tetrachloride.[7,13,19]

Electron donor	$-\Delta H$, kcal $mole^{-1}$	$-\Delta S$, e.u.	Electron donor	$-\Delta H$, kcal $mole^{-1}$	$-\Delta S$, e.u.
$C_2H_5NO_2$	1.5	7.1	N-Methylpyrrolidinone	4.0	10.9
$(CH_3)_2CO$	2.3	8.4	Benzene	3.2	9.0
$(C_2H_5)_5CO$	2.4	8.1	*p*-Xylene	2.5	6.7
$(C_4H_9)_2O$	2.3	5.3	Mesitylene	2.6	6.8
1,4-Dioxan	2.5	9.6	*p*-Diethylbenzene	2.7	7.8
$CH_3COOC_2H_5$	2.5	9.0	1,3,5-Triethylbenzene	2.5	7.9
$(C_2H_5O)_3PO$	3.8	9.6	*p*-Di-isopropylbenzene	3.3	10.3
$(CH_3S)_2$	0.9	6.6	1,3,5-Tri-isopropyl-benzene	2.9	9.8
$(CH_2)_4S$	2.3	10.2	18-Crown-6 ether	1.6	5.5
$(C_2H_5)_2S$	1.7	8.6	15-Crown-5 ether	4.0	7.5
$(C_2H_5)_3N$	4.1	15.2	12-Crown-4 ether	4.5	8.0

It has been established by NMR [7,8] that chloroform molecules are self-associated via C–H...Cl bonds. The self-association equilibrium constant K is low, amounting to 0.2 (mole fraction)$^{-1}$ at 25 °C, while the bond strength is $-\Delta H \cong 1$ kcal mol^{-1}. Chloroform dissolved in cyclohexane forms 1:1 complexes with the excess electron donor[7], because under these conditions the degree of its self-association is negligible. The thermodynamic characteristics of the hydrogen bonds

between chloroform and various electron donors are compared in Table 1. It is seen that the energies of the hydrogen bonds are low (2–4 kcal mol^{-1}) and that the strongest bonds are formed by amines.

The low degree of self-association of chloroform together with its tendency towards the preferential formation of 1:1 complexes makes it a suitable model proton donor for the study of the electron-donating properties of bases by the hydrogen bond method. The most complete data on these lines have been obtained by NMR for tertiary amines and ethers.[9] It has been shown that steric hindrance in the formation of hydrogen bonds is determined not only by the length and degree of branching of the hydrocarbon chain but also by the steric disposition of the substituents relative to the free electron pair of the heteroatom of the base. The methyl group in the β-position of the substituent hinders the approach of the proton to the electron pair. The possibility of the maximum overlap of the frontier orbitals of the proton and electron donors is then ruled out, which lengthens and weakens the hydrogen bond. For tertiary hydrogen bonds, the steric factor is most important. This is why in the series of amines there is no rigorous correlation between ΔH and Δ_C (the chemical shift due to complex formation) or $\Sigma\sigma^*$.[9]

The formation of hydrogen bonds between chloroform and phosphoryl compounds and ketones is hardly influenced by the bulk of the substituents. For this reason, a correlation is observed between ΔH and the values of $\Sigma\sigma^*$, Δ_C, or $\Delta\nu$(CH) for phosphine oxides.[10–12] Consequently the free electron pair of the donor atom, at an appreciable distance from the substituents, does not experience a steric influence by the latter.

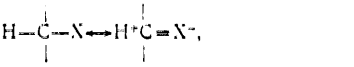
A number of studies[13–18] have been devoted to the hydrogen bonds between chloroform and π-electron donors. In the case of alkylbenzenes it was found[13] that the intermolecular interaction parameters depend in a complex manner on the electronic and steric effects of the substituents (Table 1). Contrary to expectation, the strength of the C–H...π hydrogen bonds diminishes in many instances with increase of the number of electron-donating substituents in the aromatic ring. Steric factors influence mainly the equilibrium constants. For bases whose molecules include proton-accepting centres of the π or *n* type, studies of the relative contribution of the C–H...π and C–H...*n* hydrogen bonds to the overall complex formation process are the most important.[14–18]

The proton-accepting capacity of crown-ethers has been investigated by ^{1}H NMR as a function of the number of oxygen atoms in the macroring in relation to association with chloroform.[19] The thermodynamic characteristics of the association with chloroform have been compared with data for thio- and seleno-phenols. In terms of decreasing strength of hydrogen bonds with 18-crown-6 ether, the above proton donors can be arranged in sequence Se–H ≥ S–H > C–H. An analogous sequence based on the variation of the proton-donating capacity has been observed for hydrogen bonds with electron donors of other types.[4]

For chloroform, the strength of the bond diminishes with increase of the diameter of the macroring (Table 1). In ethers with a large cavity diameter (d = 2.6 Å) the hydrogen atom involved in the bond is probably located mainly at one of the oxygen atoms. With decrease of d, the proton-accepting capacity of crown ethers increases, since the bridging hydrogen atom occupies a central or nearly central position in the cavity on formation of the complex. The possibility of an effective collective interaction of the proton charge with the dipoles of the C–O group is then ensured, which then entails the growth of the Coulombic contribution to the overall binding energy.

The proton-donating capacity of haloforms diminishes when chlorine is replaced by other halogens. The strength of the hydrogen bonds with tetrahydrofuran (THF), determined by NMR, diminishes in the sequence $Cl_3CH > Br_3CH > F_3CH > I_3CH$ ($-\Delta H$ = 3.6, 2.6, 2.4, and 1.6 kcal mol^{-1} respectively.[20] Fluoroform has a lower proton-donating capacity than chloroform and even bromoform. On the other hand, the influence of chlorine, bromine, and iodine atoms on the C–H...O hydrogen bonds corresponds to the relative electrical conductivities [sic]. The above data agree with the results of calculations by the CNDO/2 method.[21] We may recall that the strength of the hydrogen bonds between hydrogen halides and various electron donors diminishes in conformity with the variation of electronegativity on passing from F to I.[22]

There is no unaminous view in the literature about the causes of the "anomalous" influence of fluorine atoms on the proton-donating capacity of substituted methanes. It has been suggested that the deviations are caused by the greater polarisability of C–Cl bonds compared with C–F.[23] However, the main contribution to the energy of weak hydrogen bonds comes from the polarisation component and not from the Coulombic component.[24] Furthermore, the polarisability of the H–F bond is also lower than that of the H–Cl bond but hydrogen fluoride is a stronger proton donor. We believe that the explanation put forward by Creswell and Allred[20] is acceptable. According to these workers, the decrease of ΔH on passing from chloroform to fluoroform is due to the fact that, owing to the absence of *d* orbitals in fluorine atoms, resonance of the type



as a result of which the positive charge on the hydrogen atom and the polarity of the C–H bond increase, is impossible. Furthermore, the decrease of the positive charge on the hydrogen atom in fluoroform and of the proton-donating capacity of the latter, can be induced by the +*M* effect of the free electron pairs of the halogen, which is a maximum in the case of fluorine.[25] The last two factors should play a decisive role in the variation of the strength of the C–H...B bonds whose energy is determined mainly by the electrostatic interaction. The above treatment is consistent with the results of calculations by the CNDO/2 method, according to which the charge on the hydrogen atom in the chloroform molecule is much greater than in the fluoroform molecule.[25,26]

Compared with the chlorine atom, the CF_3 substituent generates a much greater positive charge on the hydrogen atom of the C–H group.[27,28] CH acids with the trifluoromethyl substituent therefore exhibit a greater proton-donating capacity. For example, the enthalpy of formation of the hydrogen bond with methylpyrrolidinone (in kcal mol^{-1}) is 4.0 for chloroform[7] and 4.7 for $CF_3CHClBr$;[30] in the case of dimethyl sulphoxide (DMSO) the corresponding values are 1.6 for chloroform[31] and 5.6 for $(CF_3)_3CH$.[29]

III. HYDROGEN BONDS INVOLVING CH GROUPS POLARISED BY ELECTRON-ACCEPTING SUBSTITUENTS

Hydrogen bonds involving CH groups polarised by powerful electron-accepting substituents such as CN, NO_2, CO_2R, SO_2R, etc. are very common. In the first place we may note that the above substituents include atoms with proton-accepting capacity. The corresponding CH acids can therefore be self-associated. However, according to NMR data the stability of the self-associated species of monosubstituted methanes is low and amounts to 0.6–1.8 kcal mol^{-1}.[30,31]

Judging from the inductive σ constants, substituents such as the cyano-, nitro-, and sulpho-groups should increase the proton-donating capacity to a greater extent than the halogens. Indeed, the introduction of the CN group into mono- and dihalogenomethanes leads to a greater shift of the stretching vibration frequency of the C–H bond than the introduction of a second or third halogen atom.[3] The enthalpies of formation of the hydrogen bonds of CH_2Cl_2, $CHCl_3$, and $CHCl_2CN$ with dioxan are 1.3, 2.4, and 3.5 kcal mol^{-1} respectively.[3] Nitromethane and chloroform form with acetone hydrogen bonds of similar strength (2.1 and 2.3 kcal mol^{-1}),[7,32] while the strength of the hydrogen bond involving 1,1-dinitroethane varies in the range 3–7 kcal mol^{-1} depending on the strength of the electron donor.[44]

However, the available data make it possible to follow only the qualitative aspect of the influence of the nature of substituents on the properties of the C–H...B hydrogen bonds. Rigorous quantitative correlation between the association parameters and the electron-accepting properties of substituents are as a rule absent. For example, according to Slasinski et al.,[34] it is possible to set up the following series based on the influence of the substituents on the association constant of methane derivatives with hexamethyl phosphoramide (HMPA): $CN \approx NO_2 > SCN > O_2NC_6H_4 > F$, Cl, Br $> CON(CH_3)_2 > CO_2R > C_6H_5$. Overall, it resembles the sequence in the variation of the σ_I, but the correlation between $\lg K$ and σ_I is very rough. There exist several possible causes of its breakdown. The proton-donating capacity of CH groups depends significantly on steric conditions, since the electron-accepting groups are in the immediate vicinity of the reaction centre. The negative charge concentrated on them hinders the approach of the base molecule to the proton of the CH group. Furthermore, with increase of the number of substituents, there is a possibility that the saturation effect, which is a progressive decrease of the substituent influence on the polarity of the C–H bond, may be manifested.[35]

quantum-chemical calculations,[25] the CF_3 substituent increases the charge on the hydrogen atom of the CH group to a greater extent than the NO_2 substituent.

Thus it is fairly difficult to predict the proton-donating capacity of the CH group polarised by electron-accepting substituents. The use of inductive constants does not yield the desired result. In individual systems it is possible to explain reasonably the experimental behaviour by resorting to data for the charges on the reaction centre.

The dependence of the characteristics of the hydrogen bonds of di- and tri-substituted methanes with electron donors of different nature on the CH acidity has been analysed.[36,37] For the hydrogen bonds of R_2CH_2 with pyridine, a parallel variation with the proton-donating capacity and acidity is observed in the main; however, in the case of DMSO the values of ΔH are almost independent of the pK_a. Malononitrile forms the weakest bond with DMSO, while in relation to pyridine its proton-donating capacity is consistent with the acidity. The reason for the above anomaly is that, apart from the hydrogen bonds, $(NC)_2CH_2$ forms dipole–dipole associated species with DMSO (according to infrared spectroscopic data[37]) by interaction between the localised dipoles of the CN and SO groups. According to the results of calculations in terms of the CNDO/2 approximation, the electron-accepting properties of the CN substituent and the proton-donating capacity of the CH group are sharply diminished in associated species of the dipole–dipole type.[38]

On passing to trisubstituted methanes (Table 3), the increase of acidity is accompanied by the enhancement of the proton-donating capacity. However, in the series of acids $HC(Y)(SO_2CH_3)SO_2C_6H_4X$ there is no single dependence of ΔH on pK_a.

Table 2. Thermodynamic characteristics of the hydrogen bonds between trisubstituted methanes and DMSO in carbon tetrachloride.[29]

R_3CH	σ_I^*	$-\Delta H$, kcal $mole^{-1}$	Δ_C, p.p.m.
{$(CF_3)_3$}CH	0.42	5.6	2.60
$(CF_3)_2$CH{NO_2}	0.63	4.8	2.34
$(CF_3)_2$CH{CN_2}	0.58	4.7	2.23
$(CF_3)_2$CH{$COOCH_3$}	0.32	3.3	1.47
{CH_3}CH$(NO_2)_2$	0	2.2	0.72

*The values of σ_I are quoted for the groups shown in braces.

Table 3. Thermodynamic characteristics of the hydrogen bonds between trisubstituted methanes $HC(COY)(SO_2CH_3)$. $(SO_2C_6H_4X)$ and DMSO and acetone (at 40 °C).[37]

X	Y	pK_a (CH_3OH)	Acetone			DMSO		
			$-\Delta H$, kcal $mole^{-1}$	$-\Delta S$, e.u.	K, (mole fraction)$^{-1}$	$-\Delta H$, kcal $mole^{-1}$	$-\Delta S$, e.u.	K, (mole fraction)$^{-1}$
Cl	C_6H_5	4.77	2.5	5.0	4.6	3.3	5.5	13.6
H	C_6H_5	5.32	2.3	4.3	4.2	3.4	6.1	12.0
CH_3	C_6H_5	5.81	2.4	5.1	4.0	3.0	5.1	10.5
Cl	OC_2H_5	5.24	2.7	5.1	6.2	2.6	4.1	8.0
H	OC_2H_5	6.06	2.3	5.6	4.5	2.6	4.5	7.0
CH_3	OC_2H_5	6.36	2.5	5.3	4.7	2.6	4.6	7.0

In our view, the magnitude of the charge on the hydrogen atom of the CH group, determined by quantum-chemical calculations, should characterise the proton-donating capacity of CH acids more fully than the inductive constants of the substituents. Analysis of the results presented in Table 2 provides a definite confirmation of the above hypothesis. Evidently, the replacement of CF_3 by NO_2 weakens the hydrogen bond despite the fact that the nitro-group has a greater electron-accepting inductive effect than the trifluoromethyl group. The reason for this is that, in conformity with

The change in the nature of the substituent Y adjoining the reaction centre alters the proton-donating capacity in parallel with the equilibrium acidity. On the other hand, the effects of the substituent X remote from the reaction centre on the proton-donating capacity and on thermodynamic acidity are not correlated. The absence of a general correlation between the proton-donating capacity of R_3CH in hydrogen bonds and acidity reflects the fact that the effects of the substituents in the molecule and in the carbanion are transmitted to the reaction centre via mechanisms of different types. In the

acid, the properties of the C–H bond are mainly determined by inductive effects, while in the carbanion there is a possibility of a mesomeric interaction.

IV. THE PROTON-DONATING CAPACITY OF UNSATURATED HYDROCARBONS

The proton-donating capacity of CH groups depends not only on the number and properties of electron-accepting substituents but also on the character of the hybridisation of the valence orbitals of the carbon atom.[3] With increase of the amount of *s* character, the proton-donating capacity also increases in view of the increase of the electronegativity of carbon and the polarity of the C–H bond. An increase of the positive charge on the hydrogen atom is observed in the series of groups

$$H-\overset{|}{\underset{|}{C}}- < H-\overset{|}{\underset{|}{C}}= < H-C\equiv \quad \text{(Ref.26)}.$$

The introduction of electron-accepting substituents naturally increases the proton-donating capacity of unsaturated compounds. Thus the substituents R can be arranged in the following sequence in terms of their influence on the constant for the association of $R_2C{=}CHR$ with HMPA:[34] $CN \simeq NO_2 > Cl > Br > C_6H_5$. An analogous sequence of substituent effects was presented above for methane derivatives.

It has been shown by NMR [30] that trichloroethylene is self-associated via hydrogen bonds of the type C–H...Cl. The stability of the species produced by its association with various electron donors varies from 1.4 kcal mol^{-1} for acetone to 4.5 kcal mol^{-1} for triethylamine (TEA).[32] The CH groups of substituted benzenes with electron-accepting substituents also exhibit proton-donating properties.[34,39,40] In the aldehydes the capacity of the hydrogen atom of the CHO group to form hydrogen bonds with DMSO, phosphine oxides, and pyridine has been observed for trichloroacetaldehyde ($-\Delta H$ = 2.4–5.2 kcal mol^{-1}).[41,42]

Acetylenic compounds form hydrogen bonds involving the π electrons of the triple bond. The enthalpy of self-association is 1.5–2.0 kcal mol^{-1}. The hydrogen bonds of monoalkylacetylenes with various electron donors are characterised by the enthalpies $-\Delta H$ = 1–3 kcal mol^{-1}.[43,44] The influence of electron-accepting substituents on the proton-donating capacity of $RC{\equiv}CH$, estimated from the increase of the chemical shift on association with acetone, increases in the following sequence of substituents R: COOH < CHO < $COCH_3$ < $COOC_2H_5$ < CN,[45] while the corresponding sequence for association with pyridine is $HO(CH_2)_2$ < $CH_3OC(CH_3)_2$ < $HOC(CH_3)_2$ < C_6H_5 < $C_6H_5OCH_2$;[46] estimation of this influence from the variation of the *K* in mixtures with HMPA led to the sequence C_6H_5 (0.15) < $BrCH_2$ (0.53) < $COOC_2H_5$ (1.66) < CN (12.1).[34] The association of phenylacetylene with ethers and thioethers has been investigated by NMR and infrared spectroscopy.[47] The values of *K* obtained by different methods agree satisfactorily. A correlation is observed between lg*K* and the $\Delta\nu$(CH).

In concluding the discussion of the properties of the C–H...B hydrogen bonds, we may note studies[23,48–49] in which the nature of the hydrogen bonds involving CH acids was investigated by quantum-chemical methods. Analysis of the redistribution of electron density (charge shift and transfer) on formation of the C–H...B hydrogen bonds showed that the bonds do not differ from O–H...B or N–H...B. The maximum contribution to the energy of the C–H...B bonds comes, as for O–H...B bonds, from the electrostatic interaction, while the polarisation contribution and the contribution due to charge transfer play a secondary role.

V. CH ACIDITY (GENERAL POSTULATES)

The reactivity of CH acids is characterised by the kinetic (k) and equilibrium or thermodynamic (pK_a) acidities. These parameters are linked by the Brønsted relation:

$$\lg k_{+(-)} = \alpha(\beta)\Delta pK_a + \text{const}, \qquad (1)$$

where

$$\Delta pK_a = pK_a(BH^+) - pK_a(CH)$$

and α and β are the reaction constants for the forward and reverse proton transfer reactions:

$$C{-}H + B \underset{k_-}{\overset{k_+}{\rightleftarrows}} C^- + HB^+. \qquad (2)$$

According to Eqn.(1), the rate of elimination of the proton should increase with increasing strength of the acid or base. The values of α and β are usually constant for a series of compounds of similar structure and $\alpha + \beta = 1$.

The Brønsted correlation is a consequence of the fundamental principle of the linear relation between the free energies of activation and of the equilibrium reaction: $\Delta\Delta G^{\neq} = \alpha\Delta\Delta G$. If it is assumed that the entropy change in the reaction series can be neglected, the above expression assumes the form

$$\Delta E = \alpha \Delta Q, \qquad (3)$$

where E and Q are the activation energy for the proton transfer reaction and the heat of the latter. It is noteworthy that the constancy of α is maintained within a relatively narrow range of values of ΔQ or ΔpK_a. For highly exothermic reactions ($\Delta pK_a \gg 0$), the activation energy for the forward process is low and $\alpha \to 0$ and $\beta \to 1$. On the other hand, for highly endothermic reactions ($\Delta pK_a \ll 0$) we have $\alpha \to 1$ and $\beta \to 0$. In the range of intermediate values of ΔpK_a the values of α and β are between 0 and 1 and $\alpha + \beta = 1$. The extent of the transitional region can be estimated with the aid of the Marcus semiquantitative theory,[50] according to which the relation between the free energies of activation and of the equilibrium reaction includes the so-called internal barrier to reaction, i.e. the value of $\Delta G^{\neq}$ corresponding to $\Delta G = 0$:

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

It follows from Eqn.(4) that

$$\alpha = d\Delta G^{\neq}/d\Delta G = \frac{1}{2}(1 + \Delta G/4\Delta G_0^{\neq}), \qquad (5)$$

$$d\alpha/d\Delta G = (8\Delta G_0^{\neq})^{-1}. \qquad (6)$$

Consequently, for symmetrical proton-exchange reactions ($\Delta G = 0$), we have $\alpha = 0.5$. With increase of the internal activation barrier, the curvature of the function $\alpha = f(\Delta G)$ or $\alpha = f(\Delta pK_a)$ diminishes and the range of values of ΔG and ΔpK_a in which α varies from 0 to 1 should broaden.[51]

The Hammond–Leffler postulate,[52,53] according to which α reflects the energy symmetry of the transition state, imparts a physical significance to the reaction constant $\alpha(\beta)$. For exothermic reactions ($\alpha < 0.5$), the structure of the transition state resembles that of the initial reactant, while for endothermic reactions ($\alpha > 0.5$) it resembles that of the product, i.e. α reflects the degree of proton transfer in the transition state of reaction (2). However, it is not yet clear whether there is a quantitative relation between α and the length or order of the bond in the C...H...B transition state.

Definite ideas concerning the structure of the transition state have arisen from the study of the kinetic isotope effect in proton transfer reactions.[1,2] It has been established experimentally that the dependence of k_H/k_D on ΔpK_a is

represented by a bell-shaped curve and reaches a maximum in the region of $\Delta pK_a = 0$, i.e. for systems to which a symmetrical transition state corresponds according to the Hammond–Leffler postulate.

On the basis of the theoretical postulate examined above, Eigen, who carried out extensive studies on protolytic reactions, proposed a classification of acids,[53] within the framework of which the large group of OH acids is regarded as "normal". The following are the features believed to be characteristic of the normal behaviour of acids:

(1) the rate of proton transfer in the thermodynamically favourable direction is limited by diffusion and is independent of ΔpK_a, i.e. $\alpha = 0$;

(2) in the reverse, slow direction, the reaction is characterised by the maximum sensitivity of the rate to ΔpK_a, i.e. $\alpha = 1$;

(3) the values of α and β differ from 0 to 1 respectively over a narrow range of values of ΔpK_a close to zero;

(4) in the transition state the proton has been almost fully transferred to the acid or base and the observed kinetic isotope effects are therefore insignificant.

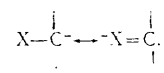
Deviations from the "normal" behaviour are characteristic of many CH acids. For example, the proton transfer even in the thermodynamically favourable direction is much slower than in the diffusion limit. Such results led to the description of CH acids as "pseudoacids". However, as will be seen below, many CH acids behave "normally", i.e. similarly to OH acids.

VI. THE ACIDITY OF HALOGEN-SUBSTITUTED HYDROCARBONS

Saturated hydrocarbons exhibit an extremely low acidity ($pK_a = 40$ for methane). In conformity with the Brønsted relation, proton transfer only to strong bases is observed and the reaction is slow.[1] The introduction of halogens sharply increases and acidity of hydrocarbons. Isotope exchange proceeds at measurable rates; alkaline but not acid catalysis is effective. The kinetics and equilibria of reactions involving proton transfer from halogen-substituted CH acids have been studied in relatively fair detail.[55–58] A general conclusion reached in the studies quoted is that a "normal" behaviour is characteristic of CH acids of this type. Thus the rate of isotope exchange involving fluoroform and chloroform in H_2O–DMSO mixtures increases, while the activation energy diminishes with increasing basicity of the medium. The kinetic results are described by the Brønsted relation ($\alpha = 0.98$). The rates of proton transfer to the carbanion are virtually the same and approach the diffusion limit. The transition state in the acid ionisation reaction probably resembles the product. The low kinetic isotope effects $k_H/k_D \leqslant 2.5$ are consistent with this hypothesis.[55]

Analogous results have been obtained for the deuterium–hydrogen exchange reactions of polyfluoro-substituted CH acids.[56] In these systems too the kinetic isotope effect was small (2.1–2.5). The transfer of the proton of the C–H bond to the methoxide ion in alcoholic solution has a high activation barrier (20–28 kcal mol^{-1}). These data indicate the antisymmetric structure of the transition state. The effect of the substituents on the equilibrium and kinetic acidities of the compounds discussed is the same, since we have $K_a \cong k_+$ when $k_- = \text{const}$.

It is noteworthy that the effect of the halogens on the equilibrium and kinetic acidities of the C–H bonds is not correlated with their electronic acitivity (Table 4) [57,58] and is probably not determined solely by the inductive effects of the substituents. According to Hine et al.,[57] the increase of acidity in the series of haloforms is due to the stabilisation of the carbanion as a consequence of the involvement of the *d* orbitals of the substituent in the delocalisation of the free electron pair:



Such resonance is impossible for fluorine owing to the absence of *d* orbitals and fluoroform is therefore least acidic. On the other hand, the increase of acidity on passing from chlorine to iodine is attributed to the greater polarisability of the orbitals of the latter.

Table 4. The rates and activation parameters of deuterium exchange involving halogenomethanes under the conditions of alkaline catalysis in aqueous solutions.[57,58]

Hal_3CD	10^4k, litre mol^{-1} s^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	pK_a
F_3CD	$1.8\cdot10^{-5}$	32.0	18.0	27
Cl_2FCD	0.89	25.9	17.7	18
$BrClFCD$	21	24.3	18.3	15
Cl_3CD	47	23.5	17.0	15
Br_2FCD	180	—	—	13
Cl_2ICD	275	22.1	15.3	13
Cl_2BrCD	290	—	—	13
$ClBr_2CD$	1435	21.3	15.6	12
Br_3CD	5790	20.3	15.0	11
I_3CD	6010	20.2	14.5	11

According to ideas developed in a number of studies,[24,59,60] the destabilising +*M* effect, induced by the repulsion between the *n* electrons of the halogens and the free electron pairs of the carbanion and, evidently, to a much lesser extent also the binding electrons of the CH group in the acid, exerts the main influence on the acidity of haloforms. This effect increases on passing from iodine to fluorine, since the amount of *p* character of the *n* electrons increases in the same sequence and their energy diminishes with decrease of the atomic radius. The changes enumerated above promote the growth of the capacity of halogens for conjugation. The observed acidity series for haloforms is fully consistent with the hypothesis of the destabilising +*M* effect of the substituents.

However, the mechanism of the influence of fluorine atoms on the properties of CH acids may vary with the position of the substituent relative to the reaction centre.[56,60] For example, on passing from fluoroform to $(CF_3)_3CH$, an increase of the kinetic acidity almost by nine orders of magnitude is observed, although the inductive constants for CF_3 and F are virtually identical. Evidently, the fluorine atoms in the β-position interact with the reaction centre only via the inductive mechanism and increase the CH acidity in conformity with their high electronegativity. On the other hand, the destabilising +*M* effect remains dominant for the fluorine atoms in the α-position (see above).

Table 5 presents data[60] which make it possible to follow the dependence of the type of influence of the fluorine atoms on the acidity as a function of their position relative to the reaction centre. It is clearly seen that only F atoms remote from the CH group increase the acidity (compounds 2, 4, and 5), while the F atoms in the α-position reduce the acidity even relative to the phenyl substituent.

Thus halogen-substituted hydrocarbons belong to "normal" acids in terms of Eigen's classification. The variation of their properties as a function of the nature or position of the halogen can be accounted for satisfactorily by the competing inductive and destabilising +*M* effects.

Table 5. The relative rates of deuterium exchange involving the compounds $(CF_3)_2CHX$ in the DMSO–MeOH system catalysed by TEA (at 37 °C).[60]

No.	X	k_{rel}	pK_a
1	C_6H_5	1	17.9
2	CF_3	4300	7
3	F	0.86	18
4	*m*-FC_6H_4	18.4	—
5	*p*-FC_6H_4	1.54	—
6	Cl	651	12.6
7	Br	2227	11.5
8	I	154	13.7

VII. THE INFLUENCE OF ELECTRON-ACCEPTING GROUPS ON THE PROPERTIES OF CH ACIDS

Electron-accepting substituents can be divided into two types. The first includes the CN, SO_2R, etc. substituents, interacting with the reaction centre of the carbanion mainly via the inductive mechanism. The second includes the COOR, COR, C_6H_5, etc. substituents, stabilising the carbanion via the conjugation mechanism. As will be seen below, the difference between the mechanisms of the influence of substituents is an important cause of the "anomalies" characteristic of many CH acids.

The CN and SO_2R ($\sigma_I = 0.58$) groups are some of the most powerful electron-accepting substituents. The acidity of the corresponding disubstituted methanes varies in the range $pK_a = 11-15$. The acid strength of the corresponding trisubstituted methanes is comparable to that of inorganic acids; for example, $pK_a = 0$ for cyanoform. Table 6 presents the results of kinetic studies of trisubstituted methanes of the type $HC(X)(SO_2R)_2$ and $HC(X)(CN)_2$.[61-63] Their analysis together with the results obtained in other studies[64,65] showed that Brønsted correlations are observed for sulpho- and cyano-methanes with X = H or alkyl and α close to unity on varying both the CH acid and the base. The rates of protonation of the carbanion are close to the rate limited by diffusion. The deprotonation of these acids is accompanied by small isotope effects: $k_H/k_D = 1.5$.[61,64,66]

Thus disulphones and dinitriles with alkyl substituents behave in deprotonation reactions as "normal" acids. Compounds with phenyl or aryl substituents are exceptions in both systems. Thus, for similar pK_a values, the kinetic acidity of the compounds with the C_6H_5 group is significantly lower (Table 6). It is noteworthy that the introduction of the phenyl group diminishes both k_+ and k_-. The above "anomalies" are not exceptional. They are characteristic also of other sulphones or nitriles containing a substituent capable of conjugation.

A significant difference between sulphones and nitriles, on the one hand, and compounds with the NO_2, COOR, COR, etc. groups, on the other, is that, while the equilibrium acidities are comparable, the latter compounds exhibit an appreciably lower kinetic acidity (Table 7) and also relatively low rates of protonation of the carbanion. Furthermore, in contrast to acids with substituents of the type Hal, CN, SO_2R, etc., the nature of the substituents in these compounds influences the rates of both the foward and reverse reactions. The coefficients α and β differ from 0 to 1 over a wide range of values of ΔpK_a. For example, the relation between $\lg k_+$ and ΔpK_a, which is common to a large number of ketones, ethers, ketoethers, and various bases, is represented by a smooth curve whose slope varies almost by a factor of 2 when pK_a changes by 25 units.[2] The kinetic isotope effect reaches a maximum in the region of $\Delta pK_a = 0$ ($k_H/k_D = 10$) and then gradually diminishes to 2 both in the region where $\Delta pK_a \cdot 0$ and the region where $\Delta pK_a \cdot 0$.

Table 6. Kinetic characteristics of the reactions involving proton transfer from disulphones and dinitriles of the type $XCH(Y)_2$ to water.[61-63]

X	Y	$10^5 k_+$, litre mol^{-1} s^{-1}	$10^{-10} k_-$, litre mol^{-1} s^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	pK_a
H	$C_6H_5SO_2$	408	2.1	—	—	11.21
C_6H_5	$C_6H_5SO_2$	1.06	0.045	—	—	12.20
H	$C_2H_5SO_2$	30.7	1.6	—	—	12.20
H	CH_3SO_2	20.6	2.3	—	—	12.55
CH_3	$C_6H_5SO_2$	1.15	2.1	—	—	13.76
CH_3	$C_2H_5SO_2$	0.063	0.73	—	—	14.56
H	CN	51.6	0.26	15.6	−20.4	11.1
t-C_4H_9	CN	0.07	0.4	18.5	−20.7	13.1
p-$NO_2C_6H_4$	CN	$0.9 \cdot 10^{-4}$	—	21.0	−30.0	13.1

Table 7. The rate and equilibrium constants for the dissociation of CH acids in water (25 °C).[67]

CH Acid	K_a	k_+, s^{-1}	k_-, litre mol^{-1} s^{-1}
CH_3NO_2	$6.1 \cdot 10^{-11}$	$4.3 \cdot 10^{-8}$	$6.8 \cdot 10^{3}$
$CH_3COCH_2CO_2CH_3$	$2.1 \cdot 10^{-11}$	$1.2 \cdot 10^{-3}$	$5.8 \cdot 10^{7}$
$CH_3CH(COCH_3)_2$	$1.0 \cdot 10^{-11}$	$8.3 \cdot 10^{-5}$	$8.3 \cdot 10^{6}$
$CH_2(CN)_2$	$6.5 \cdot 10^{-12}$	$1.5 \cdot 10^{-4}$	$2.3 \cdot 10^{7}$

It has been shown[68,69] that, in the proton exchange reactions of toluene, diphenylmethane, and their derivatives catalysed by bases of different strengths, the coefficient α varies in the range 0.31–0.75 and increases with decrease of the strength of the base. It is believed[68,69] that this is associated with the fact that the ionisation of CH acids of the above type entails a change in the hybridisation of the atomic orbitals of the carbon atom. On passing to the anion, the amount of *p* character of the orbital of the free electron pair increases, which stabilises the anion as a result of p–π conjugation with the electrons of the benzene rings.

Since the maximum overlap of the orbitals of the free electron pair and the substituent is possible for a planar configuration of the anion, the dissociation of CH acids of the type considered involve significant structural rearrangements promoting the delocalisation of the charge in the carbanion. Structural reorganisations require an energy expenditure and lead primarily to an increase of the internal activation barrier [see (Eqn.(4)]. This is why k_+ and k_- decrease and the range of ΔpK_a values in which α and β vary from 0 to 1 expands [see Eqn.(5)].

The conjugation effect, which increases the stability of the cation, does not influence to an equal extent the thermodynamic and kinetic acidities. The stabilisation of the carbanion leads to an increase of the strength of the acid and of the rate of its ionisation. However, the k_+ are then smaller than the expected value corresponding to an increase of the equilibrium acidity without taking into account the rehybridisation of the bonds and the delocalisation of the charge.[1]

One may expect that $\Delta G_0^{\neq}$ will increase and α will diminish in the region of positive ΔG with increase of the capacity of the substituents for delocalising the charge of the carbanion in the sequence $SO_2R < CN < COOR < COR < NO_2$ [70,71] [see Eqn.(5)]. The experimental results[72] presented in Table 8 are consistent with this hypothesis.

Table 8. The Brønsted coefficients for the ionisation of certain CH acids when the substituents X in the acid and in the base are varied.[72]

CH acid	Base	α
$C_6H_5CH_2CHCOCH_3CO_2C_2H_5$	XCO_2^-	0.44
$XC_6H_4CH_2CHCOCH_3CO_2C_2H_5$	$CH_3CO_2^-$	0.77
$C_6H_5CH_2CH(COCH_3)_2$	XCO_2^-	0.44
$XC_6H_4CH_2CH(COCH_3)_2$	$CH_3CO_2^-$	0.58
$C_6H_5CH_2CH(CN)_2$	XCO_2^-	1.00
$XC_6H_4CH_2CH(CN)_2$	$ClCH_2CO_2^-$	0.98

Thus the deviations of acids with substituents of the type C_6H_5, COOR, etc. from the "normal" behaviour are associated primarily with the fact that the conjugation effect makes a significant but not decisive contribution to the stabilisation of the carbanion.

The "normal" behaviour is characteristic of acids with substituents of the type CN, SO_2R, alkyl, and Hal, since their ionisation is not accompanied by a significant delocalisation of the charge and the carbanion is stabilised mainly via the inductive mechanism. Naturally, one cannot rule out the involvement of interactions of another type in stabilisation but for the CN and SO_2R substituents the contribution of resonance effects is small.[73]

VIII. THE "NITROALKANE ANOMALY"

Those CH acids whose behaviour can be regarded as "normal" or "anomalous" within the framework of Eigen's classification were examined above: the properties of both types of such acids are described by the Brønsted relation. Typical examples of systems whose behaviour does not obey the Brønsted equation are discussed below and the possible causes leading to the breakdown of the Brønsted relation are analysed.

Table 9 compares the acid properties of various diketones.[67,74] The fact that the replacement of the CH_3 group by CF_3 leads to an increase of the equilibrium acidity in conformity with the high electronegativity of the fluorine atom but the kinetic acidity diminishes at the same time is noteworthy. The coefficient $\alpha < 0$ for this system, i.e. has an "anomalous" value.

Anomalous values of the Brønsted coefficient ($\alpha < 0$ and $\alpha > 1$) are most characteristic of CH acids containing the nitro-group. Thus the equilibrium acidity of nitroalkanes increases in the sequence

$$CH_3NO_2\ (10.2) < C_2H_5NO_2\ (8.5) < (CH_3)_2CHNO_2\ (7.7)$$

(the pK_a are given in brackets), but the relative rates of abstraction of protons by hydroxide ions diminish (111:18:1) in the same sequence. The coefficients $\alpha = -0.7$ and $\beta = 1.7$ are anomalous.[75] The ionisation of alkyl-substituted nitromethanes of the type R_2CHNO_2 (where R = H, CH_3, C_3H_7, iso-C_3H_7, or t-C_4H_9) is also characterised by negative values of α.[71]

Table 9. The equilibrium and kinetic acidities of various diketones in aqueous solutions.[14,67]

CH Acid	pK_a	$10^5 k_+^T$, s^{-1}	$10^2 k_+^H$, s^{-1}	k_+^H, litre mol^{-1} s^{-1}
$(CH_3CO)_2CH_2$	8.99	66.5	1.6	$1.7 \cdot 10^7$
$CF_3COCH_2COCH_3$	6.78	33.3	1.5	$7.5 \cdot 10^2$
$(CF_3CO)_2CH_2$	5.3	15.1	—	—
$CH_3COCH_2COC_6H_5$	9.4	—	1.1	$2.7 \cdot 10^7$
$CF_3COCH_2COC_6H_5$	6.8	—	0.8	$5.5 \cdot 10^4$

Anomalies of another kind are also characteristic of nitrocompounds: the sensitivity of the kinetic acidity to the influence of substituents is greater than that of the equilibrium acidity, i.e. $\alpha > 1$. For example, $\alpha = 1.67$, 1.61, 1.42, and 1.56 have been found for nitroalkanes having the formulae

$$R(CH_2)_3NO_2,\ ArCH_2CH(CH_3)NO_2,\ ArCH(CH_3)NO_2 \text{ and } ArCH_2NO_2$$

respectively.[71,76] The reaction constant diminishes somewhat after the introduction of the chlorine atom ($\alpha = 1.23$ for $RCHClNO_2$), but the anomaly persists.[77,78] The above systems have been investigated in water and aqueous alcoholic solution. It must also be emphasised that all systems with $\alpha > 1$ included a fixed base. If the base is varied for the same nitroalkane, then the Brønsted coefficient returns to the range within the "normal" limits, i.e. $0 < \alpha < 1$.[79,80]

The hypothesis of a relation between α and the degree of proton transfer in the transition state was discussed above. The relation implies that the influence of the substituents on the transition state is intermediate between their influence on the CH acid and the carbanion. It is quite evident that in the case of nitroalkanes and similar systems, for which $\alpha < 0$ or $\alpha > 1$, such a hypothesis lacks significance.

We shall consider the general characteristics of systems for which the Brønsted coefficient has an anomalous value. In the first place we shall note that in both cases ($\alpha < 0$ and $\alpha > 1$) the effect of the substituents on k_+ and k_- is qualitatively the same. The difference is that, when $\alpha > 1$, the substituent decreases the energy of the transition state to a greater extent than that of the anion (Fig.1, curve *b*), i.e. k_+ increases faster than k_-. When $\alpha < 0$, the substituent increases the energy of the transition state but decreases that of the anion (Fig.1, curve *c*), i.e. k_- decreases to a greater extent than k_+.

The question of the causes of the anomalies described above is controversial. The influence of substituents is manifested via various effects, which in their turn make non-equivalent contributions to the energies of the transition state and the

carbanion. Thus the conjugation effect should be fully manifested only for the carbanion and can be virtually absent in the transition state. On the basis of this hypothesis, it is possible to account for the inverse relation between the kinetic and thermodynamic acidities in the series of methylnitroalkanes. The decrease of the kinetic acidity after the introduction of the CH_3 group is induced by the electron-donating inductive effect of this group, while the increase of the equilibrium acidity is caused by the stabilisation of the anion by the hyperconjugation effect.[81]

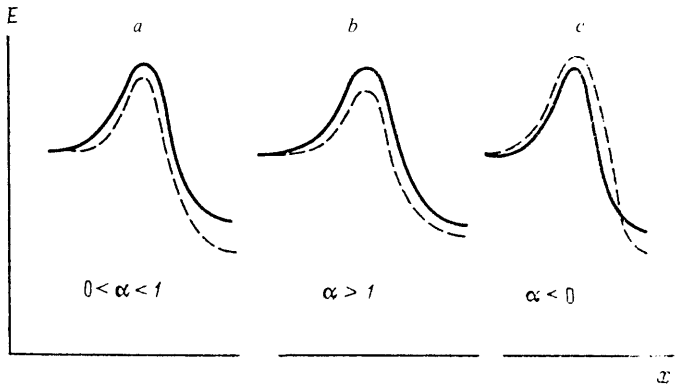
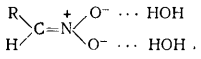


Figure 1. The effect of the introduction of a substituent on the variation of the potential energy E along the proton transfer reaction coordinate x characterised by the normal (a) and "anomalous" (b and c) values of α (continuous line—without a substituent; dashed line—with a substituent).

In aqueous alcoholic solutions specific intermolecular interactions are important apart from the intramolecular electronic effects. Solvation can stabilise the transition state and the carbanion to different extents. For example, the nitroalkane anions are stable in the ground state by virtue of solvation with which the formation of relatively stable hydrogen bonds is associated:



In this case electron-accepting substituents increase the electronic stability of the carbanion but diminish its capacity for the formation of hydrogen bonds with the solvent. Thus the influence of substituents on the anion is smoothed out. The electron-donating methyl groups promote the solvation of the anion and also increase its stability as a result of intramolecular hyperconjugation effects (see above).

In the transition state the partial negative charge is localised on the carbon atom and the solvation effects are insignificant.[79,82] The electronic effects of the substituents in the acid and in the transition state should therefore play the major role in determining the activation energy for the abstraction of a proton.[82]

The important role of solvation effects in the manifestation of "anomalies" is indicated by the following results. On passing from $ArCH_2NO_2$ to $ArCHClNO_2$, the quantity α diminishes from 1.56 to 1.23,[77,78] while for compounds of the type $ArCH(NO_2)_2$ the normal value is attained ($\alpha = 0.75$), because polynitroalkane anions hardly form hydrogen bonds with this solvent.[83]

On passing from aqueous solutions to the aprotic solvent DMSO and in the gas phase a decrease of the "anomalous" influence of the methyl groups on the equilibrium acidity of nitro-compounds is observed (Table 10).[83,84] However, the sequence of the changes in acidity with substitution remains common to all three cases. Consequently the anomaly in the constants K_a for the acids considered is caused not only by solvation but also by hyperconjugation effects.

Table 10. The change in the thermodynamic acidity $\Delta pK_a = pK_a^H - pK_a^{CH_3}$ in water, DMSO, and the gas phase on substitution of the hydrogen in nitromethane by the methyl group.[84]

CH Acid	H_2O	DMSO	Gas phase
CH_3NO_2	0.00	0.00	0.00
$CH_3CH_2NO_2$	1.80	0.68	0.5
$(CH_3)_2CHNO_2$	2.96	0.79	1.2

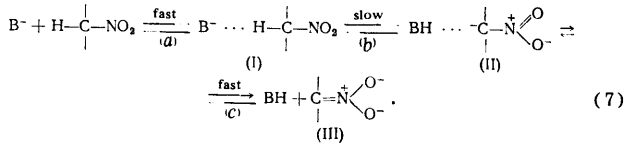
For compounds having the formula $ArCH_2NO_2$, the transition from H_2O to DMSO leads to a decrease of α from 1.56 to 0.92.[82] In DMSO the rate of dissociation decreases sharply and the heat of activation falls, which is believed[24] to be associated with the fact that the basicity of the medium increases with increasing DMSO concentration. For the given fixed acid $C_7H_5CH_2NO_2$, the change in base strength in the H_2O–DMSO mixture leads to $\alpha = 0.58$. Consequently even in the aprotic solvent the values of α determined for a fixed acid (0.58) or base (0.92) are not the same. On passing from H_2O to DMSO, the anomaly does not disappear in this system, although the extent to which it is manifested diminishes.

A formal explanation of the "nitroalkane anomaly" has been proposed by Marcus.[50,24] We may recall that, when the internal activation barrier is constant within the limits of the reaction series, α is specified by Eqn.(5) and is within the normal limits ($0 < \alpha < 1$) subject to the condition that $|\Delta G| \leq |4\Delta G_0^{\neq}|$. A change in the nature of the base should not influence $\Delta G_0^{\neq}$, so that for a fixed nitroalkane the Brønsted relation holds when the base is varied. On the other hand, when the introduction of a substituent into the acid alters the internal activation barrier, then α is specified by the expression

$$\alpha = \frac{1}{2}\left(1 + \frac{\Delta G}{4\Delta G_0^{\neq}}\right) + \left[1 - \left(\frac{\Delta G}{4\Delta G_0^{\neq}}\right)^2\right]\frac{d\Delta G_0^{\neq}}{d\Delta G},$$

whose second term can influence α significantly. The change in $\Delta G_0^{\neq}$ within the limits of the reaction series is possible either as a result of a structural reorganisation of the transition state or as a consequence of solvation effects.

According to Bordwell, who investigated various series of nitroalkanes with negative coefficients α,[71,87,88] the "nitroalkane anomaly" can be accounted for by a three-stage mechanism of the dissociation of the CH acids considered:



(7)

In the rate-limiting stage (b) the proton transfer via the $C-H...B^-$ hydrogen bond leads to the formation of a carbanion having a tetrahedral structure without a significant charge delocalisation. In the next, rapid, stage (c) the tetrahedral configuration rearranges to a planar configuration, which creates conditions in the anion for delocalisation of the charge. The influence of substituents on the rate of deprotonation of the CH acid is manifested in the slow stage involving proton transfer within the complex on passing from compound (I) to (II), while the equilibrium acidity should be determined by the effect of the substituents on the planar anion (III). There is no doubt that the structural changes in the acid influence in different ways the properties of the transition state [of stage (b)] and the anion (III). If the substituents stabilise the associated species (II) to a greater extent than the anion (III), then $\alpha > 1$; however, if the substituents have the opposite effect on the stabilities of (II) and (III), then $\alpha < 0$.

The above treatment makes it possible to throw some light onto the controversial question of the structure of the transition state in the dissociation of nitroalkanes. One must suppose that the transition state does not resemble the products, because the influences of substituents on the carbanion and on the transition state are significantly different. However, for a series of fixed nitroalkanes, $\alpha = 0.50-0.65$ and varies only slightly over a wide range of ΔpK_a as the nature of the base is varied.[79] The corresponding kinetic isotope effects are fairly large and reach a maximum near $\Delta pK_a = 0$, but in the range of ΔpK_a values greater or smaller than zero the ratios k_H/k_D vary only slightly.[87,88] The hypothesis has therefore been put forward[79] that either the transition state in the proton transfer reaction is almost symmetrical or that the quantity α and k_H/k_D are in no way related to its structure.

The above discrepancies can be eliminated when account is taken of the complex mechanism of the dissociation reaction of nitroalkanes [reaction (7)]. The quantities α and k_H/k_D should probably be referred to stage (b), the structure of the transition state of which approaches a symmetrical structure. The value of ΔpK_a for this stage is significantly smaller than that adopted in the experiment, because the latter reflects the change in the free energy throughout the entire process.[87,89]

It must be emphasised that the role of the solvation effect is significant also in the multistage mechanism,[90] because the anions of types (II) and (III) differ from one another in their capacity to form hydrogen bonds. Thus the "nitroalkane anomaly" is manifested as a consequence of the different character of the influences of the substituents on the individual stages of the dissociation process and on the solvation effects stabilising the carbanion.

In order to separate the contributions of the intramolecular electronic interactions and the solvation effects, it is necessary to study the rate of dissociation and the dissociation equilibria of CH acids in aprotic weakly polar solvents. At the present time this field of study is beginning to develop.

A detailed investigation has been made[91] of the kinetics and equilibrium in proton transfer from *p*-nitrophenylnitromethane to nitrogen-containing bases in aprotic solvents of different polarity. A parallel variation of the equilibrium and rate constants is on the whole observed for this system (with the exception of the reaction with TEA in acetonitrile): both constants increase with increase of solvent polarity and the basicity of the proton acceptor. However, no irregularities can be traced in the variation of the equilibrium or activation energy and entropy parameters. The above parallel variation is caused by combinations of the quantities $\Delta H^{\neq}$ and $\Delta S^{\neq}$, which are difficult to interpret and may be random.

Studies of the kientics of proton transfer from nitroalkane to amines in various aprotic solvents have been carried out by dynamic NMR.[92-95] In these investigations the attempts by the authors to determine separately the characteristics of the stages involving complex formation and the proton transfer proper in terms of the scheme

$$C-H + B \overset{(a)}{\rightleftarrows} C-H \cdots B \overset{(b)}{\rightleftarrows} C^- \cdots HB^+ \qquad (8)$$

are particularly interesting. Table 11 compares the results obtained. Evidently, the values of E_+ are comparable in magnitude with the heats of activation for proton transfer from *p*-nitrophenylnitromethane to amines.[91] Since both reaction (8) as a whole and stage (*b*) are thermodynamically favourable, the relations $E_+ < E_-$ holds. The anomaly is that for systems (II) and (III) the values of E_+ differ significantly for virtually equal ΔpK_a and similar values of Q. We may note that analysis of the tabulated data for system (III) leads to an unexpected result. Thus simple comparison of ΔH and E_+ shows that the energy of the transition state of the proton transfer stage is lower than the energy of the reactants. In other words the overall activation energy for the forward process in reaction (8) is negative. Under this condition, the rate of reaction should diminish with increase of temperature, which conflicts with the data of Borodin et al.[95]

Table 11. The activation energies and thermodynamic characteristics of the equilibrium in reaction (8).[92-95]

No.	CH acid	pK_a	Base	Solvent	$-\Delta H$, kcal mol^{-1}	Q, kcal mol^{-1}	E_+, kcal mol^{-1}	E_-, kcal mol^{-1}
(I)	$CH_2CH(NO_2)_2$	5.13	$NH(C_8H_{17})_2$	CCl_4	--	11	10	20
(II)	$CH_2CH(NO_2)_2$	5.13	$N(C_8H_{17})_3$	$CDCl_3$	3	12	7.9	16.9*
(III)	$(CF_3)_2CHNO_2$	5.0	$N(C_8H_{17})_3$	$CDCl_3$	6.1	12.4	4.7	11*
(IV)	$(CF_3)CH_2NO_2$	7.4	$N(C_8H_{17})_3$	$CDCl_3$	0	9	6	14

Notation: ΔH is the enthalpy of formation of the hydrogen bonds, Q the heat of reaction (8), and E_+ and E_- are the activation energies for the forward and reverse reactions of stage (b) in proton transfer.

*E_- has been determined from the formula $E_- = \Delta H - Q + E_+$.

The kinetics of proton transfer from dinitromethane to trioctylamine have been studied in aprotic solvents of different types.[94] It has been found that, with increase of the dielectric constant of the solvent on passing from cyclohexane to acetonitrile, the quantities E_+ (7.4–8.0 kcal mol^{-1}) and k_+ (27–13 s^{-1}) change insignificantly. The nature of the solvent exerts a somewhat greater influence on the heats of the equilibrium reaction, because ΔH diminishes from 4.8 to 2.2 with increasing polarity, while Q increases from 11.4 to 13 kcal mol^{-1}.

Thus, on the basis of the few date examined, one can reach the preliminary conclusion that in aprotic solvents the anomalous influence of substituents on the equilibrium and kinetic acidities of nitroalkanes diminishes but does not disappear completely.

A detailed study has been made[96,97] of the state of equilibrium and the kinetics of proton transfer from trisubstituted methanes $HC(Y)(SO_2CH_3)C_6H_4X$ (X = CH_3 or Cl; Y = COC_6H_5

or $COOC_2H_5$) to γ-collidine or TEA in methylene chloride:

$$R_3CH + N\!\!<\!\!\!

which increases the polarity of the C–H bond, and with increase of the stability of the carbanion as the energy of the orbitals of the free electron pair diminishes.

The rate of acid dissociation of ethylene and its derivatives has been scarcely investigated, since the base-catalysed proton transfer or isotope exchange reactions are accompanied by allyl rearrangements.

The hydrogen isotope exchange reactions involving benzene derivatives have been investigated.[70,98–101] It has been established that *o*-substituents accelerate the exchange (in the presence of potassium amide as the catalyst) in the sequence

$$CH_3 < H < (CH_3)_2N < C_6H_5 < CH_3O < C_6H_5O < CF_3 < F$$

and the rate of reaction is correlated with the inductive constants σ_I ($\rho = 11$). On moving away from the reaction centre, the influence of the substituents weakens and the correlation with σ_I can also break down. Thus the CF_3 group in the *m*-position accelerates the exchange to a greater extent than the fluorine atom, while the substituent CH_3O in the *p*-position diminishes the rate of exchange relative to unsubstituted benzene. These results suggest that the conjugation effect participates, apart from the inductive effect, in the stabilisation of the transition state or the carbanion. In the presence of electron-accepting substituents there is probably a possibility of the $\sigma-\pi$ interaction in the polar transition rate or in the carbanion.[98]

In the series of polysubstituted benzenes the rate of deuterium exchange increases, while the activation energy falls with increase of the number of electron-accepting substituents.[98,99] In order to understand the process mechanism, it is important to note that, when substituents in benzene or the nature of the base are varied, the results are described by the general Brønsted equation with $\alpha \approx 1$. The rates of protonation of the corresponding carbanions are independent of the structural changes ($\beta = 0$) and are similar in magnitude to the diffusion limit. Consequently, the role of conjugation in the stabilisation of the carbanion is small and the dissociation of the aryl C–H bond is not accompanied by a significant charge delocalisation and rehybridisation of the orbitals in the carbanion.[101,102]

Similar regularities are observed for acetylenic compounds. In an aqueous alcoholic medium the rate of deuterium exchange increases with increase of the inductive electron-accepting effect of the substituents in the sequence

$$HOCH_2CH_2 < HOC(CH_3)_2 < CH_3OC(CH_3)_2 < C_6H_5 < (C_2H_5O)_2CH < CH_3OCH_2.$$

Phenylacetylene remains outside the $k_+ = f(\sigma_I)$ correlation, which may be due to the resonance stabilisation of the carbanion, but the magnitude of the effect is small.[103]

The ionisation of acetylenes results in the formation of carbanions with a localised charge, since the *sp*-hybrid orbital of the free electron pair is orthogonal to the π orbitals of the triple bond and there is virtually no conjugation. The structure of the transition state resembles that of the product and the recombination of the acetylide ion proceeds at a rate which is limited by diffusion.[103–105] On the basis of the features enumerated above, substituted benzenes and acetylenes can be regarded as normal CH acids in terms of Eigen's classification.

X. THE PROTON-DONATING CAPACITY IN HYDROGEN BONDS AND CH ACIDITY

For compounds of the type $R_nX–H$ (where X are atoms of the main subgroups in Groups V–VII), it has been established reliably that, for a fixed X and variable substituents R, the strength of the hydrogen bonds X–H...B and the equilibrium acidity of the compound $R_nX–H$ vary in parallel. The same relation between the proton-donating capacity and acidity has been observed in a series of compounds R_nXH, provided that X represents atoms of elements of a single Period (X = O, N, or F). On the other hand, in the series of structurally isotypical compounds of elements of one Group but different Periods (X = N, P, As or O, S, Se) the variation of the proton-donating capacity and equilibrium acidity is antiparallel. However, for compounds with X–H groups the decrease of the proton-donating capacity is as a rule accompanied by a fall of kinetic acidity.[4]

For CH acids, virtually no comparisons have been made of the proton-donating capacity in hydrogen bonds and the thermodynamic and kinetic acidities. It has only been suggested[2] that the relatively low rates of ionisation of CH acids are caused by the weak capacity of the CH groups for the formation of hydrogen bonds. The data available at present make it possible to consider the relation between the proton-donating capacity and the CH acidity in greater detail.

It has been established[20,106] that the strength of the C–H...B hydrogen bonds between haloforms and electron donors of different types diminishes in the sequence

$$Cl_3CH > Cl_2BrCH > Br_3CH > F_3CH > I_3CH$$

and, with the exception of fluoroform, is correlated with the electronegativity of the halogens. The kinetic acidity diminishes on passing from iodoform to fluoroform:

$$I_3CH > Br_3CH > Cl_2BrCH > Cl_3CH > F_3CH \text{ (Refs.57–58).}$$

The replacement of one of the halogen atoms by a more complex electron-accepting substituent does not alter the above sequences.[34,80] Thus the variation of the proton-donating capacity in the formation of hydrogen bonds and of the kinetic acidity of compounds containing halogen atoms is antiparallel. If account is taken of the fact that in the series of compounds considered the variation of the kinetic and equilibrium acidities obeys the Brønsted equation, it becomes clear that the variation of the proton-donating capacity and of the thermodynamic acidity is antiparallel.

The above features are due to the fact that the proton-donating capacity in hydrogen bonds is determined primarily by the polarity of the CH bonds, which depends in its turn on the electronegativity of the halogen. Fluoroform, in the molecule of which the positive charge on the hydrogen atom is minimal because the +*M* effect is a maximum for fluorine, is an exception. On the other hand, the acidity of haloforms is determined mainly by the stability of the carbanion, determined by conjugation involving the *d* orbitals and the +*M* effect.[1]

The CF_3 group, interacting with the reaction centre of the acid and the anion predominantly via the inductive mechanism, has a parallel influence on the proton-donating capacity and the kinetic acidity. Thus the replacement of the chlorine atoms by the CF_3 groups increases the strength of the hydrogen bonds with DMSO from 1.6 kcal mol^{-1} for chloroform to 5.6 kcal mol^{-1} for $(CF_3)_3CH$ [28,29] and accelerates the deuterium–hydrogen exchange [the constants k_+ for the compounds $(CF_3)_2C_6H_5CH$, CF_3CHCl_2, $(CF_3)_2CHCl$, and $(CF_3)_3CH$ are in the ratios 1 : 2.3 : 651 : 4290].[60]

The substitution of the CF_3 group by the strong electron-accepting substituents NO_2 and CN strengthens the acidity but reduces the proton-donating capacity (Table 13). It is of interest to note that, for compounds (II) and (IV), which have similar equilibrium acidities, the activation energies for the abstraction of a proton are correlated with the strength of the hydrogen bonds. Presumably in the systems discussed the structure of the transition state is more like that

of the initial hydrogen-bonded molecular complexes than that of close ion pairs. This probably constitutes the cause of the parallel influence of substituents on the proton-donating capacity and the kinetic acidity.

Table 13. The enthalpies of the hydrogen bonds with DMSO and the activation energies for proton transfer from CH acids to amines.[1,29,93,94]

No.	CH acid	pK_a	$-\Delta H$, kcal mol^{-1}	E_+, kcal mol^{-1}
(I)	$(CF_3)_3CH$	7.0	5.63	—
(II)	$(CF_3)_2CHNO_2$	5.0	4.82	4.7
(III)	$(CF_3)_2CHCN$	0	4.75	—
(IV)	$CH_3CH(NO_2)_2$	5.2	2.23	7.9

In the series of dinitriles, parallel changes in the formation constants of the hydrogen bond and the equilibrium as well as kinetic acidities are observed. The introduction of a bromine atom into the malononitrile molecule increases the acidity and proton-donating capacity, while the introduction of the phenyl group diminishes these quantities (Table 14). The nature of CN substituents is such that they influence the reaction centres of the acids and anion via a single mechanism—the inductive mechanism (see Section VII). The introduction of these groups therefore leads to a parallel variation of the polarity of the C–H bonds and of the stability of the carbanions.

Table 14. The formation constants of the hydrogen bonds with HMPA and dimethylformamide (DMF) (in carbon tetrachloride) and the relative rate constants for the ionisation (in H_2O) of a series of dinitriles.[34]

CH Acids	K, litre mol^{-1} (HMPA)	K, litre mol^{-1} (DMF)	pK_a	k_+^{**}
$CHBr(CN)_2$	205	—	7.8	10^8
$CH_2(CN)_2$	60	11.4	11.1	10^6
$C_6H_5CH(CN)_2$	—	5.28	13.1*	1*

*The values of pK_a and k_+ are quoted for the compound $O_2NC_6H_4CH(CN)_2$.[63]
**The constant k_+ has been estimated from the data of Hibbert and co-workers.[62,63]

In the series of trisubstituted methanes of the type $HC(Y)(SO_2CH_3)SO_2C_6H_4X$ there is no general relation between the thermodynamic or kinetic acidity and the strength of the hydrogen bonds with electron donors (Table 12). A change in the nature of the substituent Y adjoining the reaction centre induces a change in the proton-donating capacity, which is in parallel with the change in the equilibrium acidity but is antiparallel in relation to the kinetic acidity. Within a series of isotypical compounds (for a fixed Y), the influence of a remote substituent X on the proton-donating capacity agrees better with its influence on the kinetic acidity than on the equilibrium acidity. These relations are caused by the initial reactant-like structure of the transition state in the dissociation reactions of the CH acids considered, whose energy, like the polarity of the C–H bonds, is determined mainly by the inductive influence of the substituents.

The proton-donating capacity and acidity of substituted bezenes increase after the introduction of electron-accepting substituents. Thus an increase of the number of chlorine atoms from 3 to 5 leads to an increase of the constant for association with HMPA [34] and to a decrease of pK_a from 34 to 30.[107] Since $\alpha = 1$ and $\beta = 0$ ($k_- = \text{const.}$) for substituted benzenes and K_a is therefore proportional to k_+, one may expect a correlation of the proton-donating capacity not only with the thermodynamic acidity but also with the kinetic acidity.

The character of the variation of the proton-donating capacity of the acetylenic compounds $RC{\equiv}CH$ can be inferred from the chemical shift of the signal due to the CH protons in associated species with pyridine,[48] which increases in the following sequence of substituents R:

$$HO(CH_2)_2<HOC(CH_3)_2<CH_3OC(CH_3)_2<C_6H_5<(C_2H_5O)_2CH.$$

The deuterium exchange rate constants increase in the same sequence.[103] Evidently, the inductive influence of R determines the proton-donating capacity and the kinetic or equilibrium acidity of the acetylenic compound, since the *sp*-hybrid orbital of the free electron pair in the acetylide ion is orthogonal with respect to the π orbitals and there are no effects of conjugation with the substituent. This applies also to the transition state whose structure resembles that of the product.[105]

Thus among CH acids there are a series of compounds differing in the character of the relations between the proton-donating capacity in hydrogen bonds and the acidity. These differences are caused primarly by the fact that the influence of substituents on the properties of CH acids discussed is exerted via mechanisms of different nature. Thus the proton-donating capacity of CH groups depends on their polarity and is therefore determined mainly by the inductive effect of the substituents. The equilibrium and kinetic acidities depend both on the inductive and mesomeric effects of the substituents. The predominance of particular mechanisms of the substituent influence is associated both with the structure of the acid and the carbanion and with the structure of the transition state.

Since the C–H...B hydrogen bonds are located on the coordinate of the deprotonation reaction of CH acids, we shall attempt in the first place to determine the relations between the proton-donating capacity in hydrogen bonds and the kinetic acidity. Analysis of the results presented above suggest that a parallel variation of ΔH and k_+ or E_+ should be observed in a series of acids for which the kinetic and equilibrium acidities are determined by the polar effects of the substituents which are virtually incapable of mesomeric interaction; either the transition state in the transfer of the CH proton resembles the initial reactant and the substituents of any type influence the kinetic acidity mainly via the inductive mechanism or the transition state of the reaction has a structure close to that of the carbanion, but the conditions for conjugation between the free electron pair and the substituents are lacking for steric reasons.

Evidently, when the Brønsted relation holds in the series of CH acids satisfying the conditions indicated, then the proton-donating capacity should be correlated not only with the kinetic acidity but also with the thermodynamic acidity.

The correlation between ΔH and $k_+(E_+)$ breaks down if a transition state, to the stabilisation of which the effects of the conjugation between the reaction centre and the substituents make a significant contribution, corresponds to the

deprotonation of the CH acids. Presumably in reaction series of this kind the form of the potential curve corresponding to the extension of the C–H bond depends on the nature of the substituent.

In comparing the properties of the C–H...B bonds and the CH acidity, we did not consider the questions of the properties of the $C^-...HB^+$ hydrogen bonds. In aprotic solvents these bonds determine in many respects the stability of the ion pair, while in protic solvents (SH) bonds of the type $C^-...HS$ play a significant role in solvation effects. Thus the problem arises of the relation between the electron-donating (proton-accepting) capacity of the carbanions in hydrogen bonds and their kinetic stability (basicity). However, there are so far virtually no literature data necessary for such a comparison. Experimental and theoretical study of hydrogen bonds involving carbanions is therefore urgently required.

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