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Equilibrium Acidity of Carbon - Hydrogen Bonds in Organic Compounds

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A survey is made of experimental results on the equilibrium acidity of CH acids in the gas phase and in aqueous solution, as well as in dimethyl sulphoxide, cyclohexylamine, benzene, ether, and other aprotic solvents. Reasons are discussed for the sharp difference between CH and OH acids that appears on passing from the gas phase to aqueous solutions. Various acidity scales for CH acids in aprotic solvents—the McEwen, Streitwieser, Cram, Breslow, and polarographic scales, and the acidity scale in dimethyl sulphoxide—are compared. A list of 114 references is included.

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I. INTRODUCTION

Under the influence of a base (a proton acceptor) of suitable strength almost all organic compounds are capable of ionising with the formation of carbanions, i.e. negatively charged species in which the charge—or more often part of the charge—is concentrated on a carbon atom. This permits the occurrence of a multitude of organic reactions—e.g. carbonyl–methylene condensations, transmetallations, allyl rearrangements under the influence of bases, etc.—in which the limiting step is detachment of a proton. Even saturated hydrocarbons exhibit acidic properties, though fairly weak[1]. Several reviews have recently appeared on CH acids and carbanions[2-4], among which Cram's monograph[2] is of primary importance.

In the present paper we shall use the term *acidity* instead of the alternative "acid ionisation constant", in order to stress the connection

$$RH + B^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^- + HB;\ pK_a = -\lg K_a = -\lg \frac{k_1}{k_{-1}}$$

between the *equilibrium* (thermodynamic) acidity, i.e. the acid ionisation constant K_a, and the *kinetic* acidity, i.e. the rate of detachment of a proton from the molecule of the acid k_1. A linear relation is quite often observed between equilibrium and kinetic acidities, i.e. between pK_a and $\lg k_1$, when Brønsted's principle is valid. We shall consider only data on the equilibrium acidity of CH acids, which is independent of the mechanism of detachment of the proton and best represents the thermodynamic stability of carbanions in a given system. Since a correction for the energy of solvation should be made to the energy of every species involved in acid–base equilibrium in solution, we shall first examine the acid–base equilibrium in the gas phase, which best corresponds to the "intrinsic" acidity of the CH acid and is due solely to structural factors. Acid–base equilibrium in various solvents will be discussed subsequently.

II. ACID IONISATION IN THE GAS PHASE AND IN WATER

1. Acidity in the Gas Phase

The acidity of any acid in the gas phase can in principle be determined from the thermodynamic cycle[3,5]

$$\begin{array}{c} AH \rightarrow A^{\cdot} + H^{\cdot};\ DH \\ A^{\cdot} + e^- \rightarrow A^-;\ -EA \\ H^{\cdot} \rightarrow H^+ + e^-;\ IP \\ \hline AH \rightarrow A^- + H^+;\ \Delta H = DH - EA + IP \end{array}, \qquad (1)$$

where DH is the A—H dissociation energy, EA the electron affinity of the A· radical, IP the ionisation potential of the hydrogen atom, and ΔH the enthalpy of ionisation of the acid. Investigation of the dependence of acidity on the structure of the acid is of the greatest interest for organic chemistry. With such an approach the ionisation potential IP cancels out, and the variation in acidity in a series of CH acids can be predicted from a knowledge merely of DH and EA.

Brauman et al.[5], as well as several other workers[6], have used pulsed ion–cyclotron resonance to determine experimentally the electron affinities of several radicals, and have then employed the thermodynamic cycle (1) to calculate values of ΔH for the ionisation of the hydrides of several elements. The results (Table 1) indicate[5] that the acidity of hydrides in the gas phase increases from left to right in a period, and downwards in a group:

$$\begin{array}{ccccccccc} CH_4 & < & NH_3 & < & H_2O & < & HF \\ \wedge & & \wedge & & \wedge & & \wedge \\ SiH_4 & < & PH_3 & < & H_2S & < & HCl \\ & & \wedge & & \wedge & & \wedge \\ & & AsH_3 & < & HBr & & \\ & & & & \wedge & & \\ & & & & HI & & \end{array}.$$

The main factor determining the variation relative acidity is the electron affinity along a period, and the dissociation energy down a group (Table 1). A ready explanation of

this rule is that the A—H molecular orbital ψ is a combination of the atomic orbitals φ_A and φ_H, and will be the more stable relative to φ_A the closer the energies of φ_A and φ_H, i.e. the smaller the difference in electronegativity between the given element and hydrogen. With increase in the electronegativity of the element φ_H becomes more stable, the mixing coefficient of the orbitals decreases, and the energy of ψ approaches that of φ_A. Since Pauling's electronegativity shows a greater variation along a period than down a group and is a function of the electron affinity, the acidity of hydrides will be more strongly dependent on *EA* along a period than down a group in the Periodic System.

Table 1. Bond dissociation energies, electron affinities, and calculated enthalpies of ionisation for simple hydrides in the gas phase[5,6] (ionisation potential of hydrogen *IP* = 316 kcal mole^{-1}).

Hydride	*DH*	*EA*	ΔH	Hydride	*DH*	*EA*	ΔH
	kcal mole^{-1}				kcal mole^{-1}		
CH_4	104			H_2S	90	53	350
NH_3	110	17	407	HCl	103	83	333
H_2O	119	42	390	AsH_3		29.3	
HF	136	80	370	HBr	88	78	324
SiH_4	80			HI	71	71	314
PH_3	80	28.8	364				

The weakest acid among the above examples is methane; this in particular is a consequence of the low electron affinity of the methyl radical. However, replacing a hydrogen atom in methane by a group which increases the electron affinity of the corresponding radical, i.e. which stabilises the carbanion, leads to an increase in the acidity. Introduction of the inductively electronegative chlorine makes the enthalpy of ionisation for the carbon—hydrogen bond smaller than the value for ammonia: $CH_3Cl > NH_3 > CH_4$. Toluene, whose phenyl group stabilises the negative charge by a conjugation mechanism, is a stronger acid than is water[7].

Existing experimental results can be summarised by the sequence

$$n\text{-}C_4H_9SH > CH_3NO_2 > \text{cyclo-}C_6H_6 \geqslant CHCl_3 > CH_3COCH_3 > CH_3CN > CH_2Cl_2,\ CH_3SOCH_3 \geqslant C_5H_6,\ t\text{-}C_4H_9OH,\ i\text{-}C_4H_9OH > C_2H_5OH > CH_3OH > C_6H_4,\ C_6H_5CH(CH_3)_2 > C_6H_5CH_3 > C_3H_8 > H_2O > C_6H_6 > H_2 > NH_3 > C_2H_4,\ C_6H_{12} > (CH_3)_3,\ CH_4$$

in which various Brønsted acids are arranged in order of diminishing acidity (in the gas phase in a flowing afterglow at 300°K).[8] This sequence evidently destroys completely our usual ideas of the relative acidities of various compounds, based on the study of aqueous or alcoholic solutions.

It is interesting that in the gas phase alkyl substituents increase the acidity of a molecule: i.e. like halogens they possess a $-I$ effect. Thus the acidity of alcohols in the gas phase increases in the opposite sequence

propan-2-ol > ethanol > methanol > water

to the acidity of the same compounds in aqueous solution[9,10]. The reason is, of course, solvation. The ionisation of hydrogen chloride, for example, is endothermic in the gas phase (ΔH = +333 kcal mole^{-1}—Table 1), but in water ΔH = −16 kcal mole^{-1}.[11]

The energy parameters listed in Table 1, as well as the qualitative series given in the text, show that no sharp distinction exists between CH acids and other types of acids in the gas phase. This is indicated also by Ritchie and King's theoretical calculations[12] of potential-energy surfaces for a series of simple gas-phase proton transfers from the molecules—hydrogen, hydrogen fluoride, water, ammonia, and methane—to the hydride ion. As expected, the lowest energy corresponded in every case to that reaction path involving attack by the hydride ion along the axis of the X—H bond:

$$X\text{—}H \leftarrow\ -\ -H^- \quad (X = H,\ F,\ OH,\ NH_2,\ CH_3)\ .$$

Water, ammonia, and methane were found to behave similarly, the only distinction between them consisting in a quantitative energy difference between reactants and products of proton transfer.

Thus hydrocarbons and their derivatives (i.e. CH acids) are inherently just as likely to exhibit acid properties as are hydrides of other elements and their substituted derivatives†. In hydroxylated solvents, however, the acidic properties of hydrides and substituted hydrides of electronegative elements (e.g. hydroxyl acids) are far more strongly developed than are those of CH acids. It has now been found that the ability of hydroxylated solvents to promote the acid ionisation of hydrides of electronegative elements is due to their specific property of forming hydrogen bonds with these elements. In the next subsection we shall compare the acidities of CH and OH acids in water.

2. Acidity of CH Acids in Water—Comparison with OH Acids

In the gas phase toluene possesses more strongly developed acidic properties than does water[7]. We shall examine what occurs in the acid ionisation of these two compounds in a hydroxylated solvent. Acid—base equilibria in the two systems can be written

$$H_2O\cdot solv. + B\cdot solv. \rightleftharpoons HB^+\cdot solv. + OH^-\cdot solv.$$
$$PhCH_3\cdot solv. + B\cdot solv. \rightleftharpoons HB^+\cdot solv. + PhCH_2^-\cdot solv.$$

The calculation of ionisation constants in solution must take into account the solvation of all species involved in the equilibrium, on both sides of the equations. If the proton acceptor B is the same in these two examples and reaction takes place in the same solvent, calculation of the relative acidity of water and toluene in solution will allow for the solvation energies only of water and toluene on the left-hand side of the equilibria, and of hydroxide and benzyl anions on the right-hand side.

The difference between the solvation of water and that of toluene in hydroxylated solvents is due to the fact that the latter solvate molecules and anions mainly by hydrogen bonding. Eigen gives the sequence

$$OH\cdots O > OH\cdots N,\ NH\cdots O > NH\cdots N > SH\cdots X,\ RH\cdots S > PH\cdots X,\ XH\cdots P > CH\cdots X,\ XH\cdots C$$

(where X is any element) of diminishing ability of elements to form hydrogen bonds[13], with OH and CH acids located at opposite ends: the former are the strongest, and the latter the weakest, hydrogen-bond donors. Hence on passing from the gas phase to a hydroxylated solvent,

† Acetic acid, for example, can be regarded as oxygen hydride substituted by an acetyl group.

e.g. water, the energy of the water molecule shows a greater decrease than that of the toluene molecule. Similarly, oxygen bases are the strongest, and carbon bases the weakest, hydrogen-bond acceptors. On passing from the gas phase to aqueous solutions, therefore, the energy of a hydroxide ion will also decrease far more strongly than that of a benzyl anion.

The principal factor determining the relative acidity of water and toluene in water is the difference between the solvation of the anions. According to results obtained by Parker[14] the most important energy contribution in reactions and equilibria involving anions is made by the difference in solvation of the anions on passing from an aprotic to a protic solvent (in the present case from the gas phase to water). The hydroxide ion, which is small and has a localised charge, is strongly solvated by water, whereas the benzyl anion, with a delocalised charge, is more poorly solvated‡. Hence it follows that the difference between the solvation energies of the hydroxide ion and of water considerably exceeds the difference between those of toluene and the benzyl anion: in other words, a hydroxylated solvent promotes strongly the process $H_2O \rightarrow OH^-$ and only weakly the process $C_6H_5CH_3 \rightarrow C_6H_5CH_2^-$. As a result, equilibrium involving water is far more strongly displaced to the right than the equilibrium involving toluene, in water compared with the gas phase, an effect illustrated by Table 2.

Table 2. Effect of solvation on change in relative acidity of water and toluene on passing from the gas phase to aqueous solution.

Molecule or ion solvated		Net change in acidity
H_2O	OH^-	
well	very well	strong increase
$PhCH_3$	($PhCH_2^-$)	
poorly	(poorly)	slight*

*The anion is therefore "instantly" protonated in water.

Thus solvation effects greatly enhance the acidity of water in aqueous medium, whereas toluene does not exhibit acid properties. This leads to the conclusion that the benzyl anion is "strongly basic", although it would be more correct to say "strongly basic in water", since in the gas phase all bases are strongly basic, as we have already seen.

The above example enables us to understand why, in water, CH acids are far weaker than OH acids. This is further illustrated in Table 3, which compares the acidities of acids of the two types of similar structure. It may be concluded that CH acids in water are on the average weaker than the corresponding OH acids by $\Delta pK_a = 20$.

However, some CH acids are quite strong even in water (pK_a values in Table 4). Appreciable dissociation in water is shown only by those CH acids which contain so called *acidifying* groups such as nitro, acyl, cyano, etc., capable of stabilising the carbanions formed by dissociation. The introduction of more than one such group adjacent to the ionised bond leads to a still greater increase in acidity. The ionisation constants of such CH acids in water can be determined by the usual methods--potentiometrically, spectrophotometrically, conductometrically, etc.

‡ This follows also from Pearson's principle of hard and soft acids and bases[15].

Table 3. Effect of substituents on acidity ($pK_a = -\lg K_a$) of related hydroxyl and methine acids (difference in acidity ΔpK_a) determined from the equilibria (other than methane):

$$H-OR + H_2O \rightleftharpoons OR^- + H_3O^+$$
$$H-CH_2R + H_2O \rightleftharpoons CH_2R^- + H_3O^+$$

Acid	pK_a	Ref.	ΔpK_a	Acid	pK_a	Ref.	ΔpK_a
H—OH	15.7	2	25	H—OCN	3.7	17	20
$H-CH_2NO_2$	40*	2		$H-CH_2CN$	24	2	
$H-OCOCH_3$	4.7	16	16	$H-ONO_2$	(−7)	18	(17)
$H-CH_2COCH_3$	21	2		$H-CH_2NO_2$	10.2	(Table 4)	

*On Cram's scale (Section III, 2).

Table 4. Acidity of CH acids in water at 25°C.

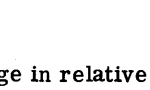
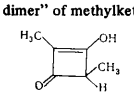
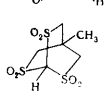
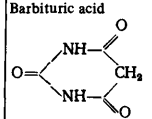
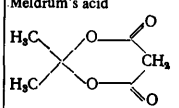
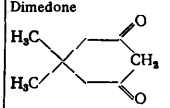
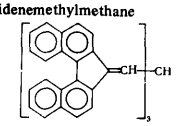
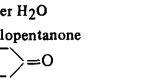
No.	Compound	pK_a	Determination	Ref.
1	Pentacyanocyclopentadiene 	(<−11)	spectroscopic	19
2	Tricyanomethane $CH(CN)_3$	(−5.13)	spectroscopic	20
3	Trinitromethane $CH(NO_2)_3$	0.17	spectroscopic, at 20°C	21
4	"Acid dimer" of methylketen 	2.8	potentiometric	22
5		3.30	potentiometric	23
6	Dinitromethane $CH_2(NO_2)_2$	3.57	conductometric, spectroscopic	24, 25
		3.60	spectroscopic at 20°C	26
		3.47	spectroscopic at 20°C	27
7	Barbituric acid 	4.0 (pure CH acidity)	relaxation	28
8	1,1,1-Trifluoropentane-2,4-dione $CF_3.CO.CH_2.CO.CH_3$	4.7	potentiometric	29
9	Meldrum's acid 	4.83 (mixed acid) enol 2.49	relaxation	28
10	1,1-Dinitroethane $CH_3CH(NO_2)_2$	5.21	spectroscopic	26
11	Nitroacetone $CH_3.CO.CH_2.NO_2$	5.1	potentiometric	29
12	Dimedone 	5.23 (pure enol)	spectroscopic	30
13	Cyclohexane-1,3-dione 	5.26	conductometric	31
14	Triacetylmethane $CH(COCH_3)_3$	5.81	potentiometric	32

Table 4 (contd.)

No.	Compound	pK_a	Determination	Ref.
15	Tris-7*H*-dibenzo[*c,g*]fluorenylidenemethylmethane 	5.9	spectroscopic	33
16	Ethyl fluoronitroacetate $NO_2CHF.COOC_2H_5$	6.28	spectroscopic	34
17	Phenylnitromethane $C_6H_5CH_2NO_2$	6.8 aci-form 3.89	potentiometric, polarographic	35
18	Dibenzoylmethane $C_6H_5COCH_2COC_6H_5$	8.95	spectroscopic	36
19	$(CH_3)_2\overset{+}{S}-CH_2-\overset{+}{S}(CH_3)_2$	9.00	potentiometric	37
20	Pentane-2,4-dione $CH_3COCH_2COCH_3$	8.94 enol 8.13	spectroscopic	30, 32
21	Nitromethane CH_3NO_2	10.21 10.24 10.1	potentiometric potentiometric spectroscopic	38 39 40
22	Ethyl acetoacetate $CH_3COCH_2COOC_2H_5$	10.49 enol 8.09	potentiometric at 20°C	30
23	Malononitrile $CH_2(CN)_2$	11.19	potentiometric	29
24	Diphenylsulphonylmethane $C_6H_5SO_2CH_2SO_2C_6H_5$	11.21	spectroscopic	41, 42
25	Ethyl malonate $CH_2(COOC_2H_5)_2$	13.30	potentiometric	29
26	Water H_2O	15.7		
27	Cyclopentanone 	16.7 enol 11.8	bromine method	43
28	Tri-*p*-nitrophenylmethane $(p\text{-}NO_2C_6H_4)_3CH$	17.44 (in alcohol)	potentiometric	44

The CH acids listed at the start of Table 4 are comparable in strength with mineral acids, e.g. hydrochloric and sulphuric acids. The weakest CH acid whose acidity could be measured in aqueous solution (cyclopentanone) has $pK_a = 16.7$. It is noteworthy that Table 4 contains barely a single "pure" hydrocarbon, i.e. a CH acid containing no acidifying group. The only exception is Kuhn's hydrocarbon (No. 15), but it occupies a special position, since the dibenzofluorenylidenemethyl group is a strongly acidifying substituent (other such groups and their effect on acidity have been discussed[33]).

Water is unsuitable as a solvent for determining the equilibrium acidity of alkanes, alkenes, arenes, cycloalkanes, and other hydrocarbons. It is not in general an ideal solvent for studying the ionisation equilibria of CH acids, since it has in water a fairly high acidity (for H_2O in water $pK_a = 15.7$). Methods have therefore been developed for determining the acidity of hydrocarbons in aprotic solvents, and will be considered below.

III. METHODS FOR DETERMINATION OF IONISATION EQUILIBRIUM OF CH ACIDS

The equilibrium acidity is determined by the position of equilibrium between acids and conjugate bases. Most of the data on the equilibrium acidity of hydrocarbons have been obtained from the study of *transmetallations*

$$R-H+R'-M \rightleftarrows R-M+R'-H$$
(M=Li, Na, K, Cs; R=Alk, Ar, Aralkyl, etc; R'=Alk, Ar, cyclo-$C_6H_{11}NH$, NH_2, etc.)

in solvents of low polarity and low proton-donating activity (ether, benzene, liquid ammonia, cyclohexylamine, dimethyl sulphoxide, etc.).

In 1908 Shorygin showed that ethylsodium metallates benzene, toluene, and diphenylmethane[45], which indicated that ethane was a weaker acid than the latter three hydrocarbons. Many similar qualitative results have since been obtained: it was shown[46], for example, that potassamide in liquid ammonia metallates diphenylmethane but not toluene, pentylsodium reacts with benzene, and phenylsodium in turn reacts with toluene[47]. These results enabled the sequence of increasing acidity to be constructed[48]:

pentane (or ethane) < benzene < toluene < ammonia < diphenylmethane.

Gilman et al. established that the yield of transmetallation product obtained with dibenzothiophen depends on the nature of the organolithium compound RLi with which it reacts (Table 5).[49] These results show that the acidity of the hydrocarbons RH should increase in the above sequence.

Table 5.

R	n-C_4H_9	C_6H_5	1-$C_{10}H_7$	p-$CH_3OC_6H_4$
Yield, %	55	12	7.6	0

By the end of the 1930s many data of this type had been obtained[50-54], enabling a qualitative assessment to be made of the relative strengths of CH acids. However, quantitative comparison of CH acidities began only with the work of Conant and Wheland[55,44,57] and of McEwen[56]. These papers are now regarded as classics.

1. Quantitative Assessment of Acidity of Weak CH Acids

Conant and Wheland[55] used a colorimetric method and the carboxylation of organosodium and organopotassium compounds to estimate the relative acidity of hydrocarbons; McEwen also used polarimetry[56]. This work involved study of the equilibrium of the sodium or potassium salts of the CH acids

$$R-M+R'H \underset{\text{ether or benzene}}{\overset{25^\circ}{\rightleftharpoons}} R-H+R'-M \qquad (2)$$

in ether by Conant and Wheland, in benzene by McEwen. The salts RM and R'M absorb at different wavelengths, so that their concentrations can be estimated colorimetrically. The change in colour usually occurs rapidly, but in some cases, especially when sodium salts are used, many days are required to reach equilibrium. The equation

$$pK_a(RH) - pK_a(R'H) = -\lg\frac{[RM]}{[RH]} + \lg\frac{[R'M]}{[R'H]} \qquad (3)$$

holds for the equilibrium (2). McEwen originally assumed that the salts RM and R'M were dissociated to the same extent, whereas the CH acids were not dissociated at all. With these postulates formula (3) becomes

$$pK_a(RH) - pK_a(R'H) = -\lg\frac{[R^-]}{[RH]} + \lg\frac{[R'^-]}{[R'H]}.$$

It was subsequently shown, however, that at 25°C the sodium and caesium salts of fluorene exist as internal ion-pairs, whereas the lithium salt occurs as separated ion-pairs, which have the same spectrum as intimate

ion-pairs in the visible region, but differ in the ultraviolet spectrum[58]. Electrical conductivity data show that these fluorene salts are only slightly dissociated. Thus the change in colour observed by McEwen is due to the formation not of dissociated compounds but of ion-pairs: i.e. Eqn. (3), proposed by Cram[2], is valid.

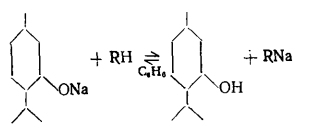
It follows from Eqn. (3) that, with equal initial concentrations of RM and R'H, visual observation of 91% (more precisely 90.9%) metallation will correspond to a difference between the acids RH and R'H of $\Delta pK_a = 2$. If such a degree of metallation is reached with a fivefold excess of R'H, the corresponding difference between the acids will be only 0.4.

McEwen compared various pairs of CH acids, which involved many cross experiments. An additional method of checking the correctness of the colorimetric results was provided by carbonation. The position of equilibrium between two acids and their salts was assessed from the relative yield of carboxylic acids obtained after carbonation of the equilibrium mixture

$$\begin{array}{ccc} RH + R'M & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & RM + R'H \\ \downarrow CO_2\ k_2 & & \downarrow CO_2\ k_3 \\ R'COOM & & RCOOM \end{array} \quad (4)$$

Obviously, the method is applicable only when both $k_2 \gg k_1$ and $k_3 \gg k_1$ (Eqn. 4). The two methods gave mutually consistent values of ΔpK_a for various pairs of CH acids.

McEwen used a polarimetric method to determine the position of equilibrium between sodium mentholate and various CH and OH acids, as well as between menthol and the sodium salts of the CH and OH acids (in benzene):



$[\alpha]_D^{23} = -12.2°$ Na *laevo*-mentholate

$[\alpha]_D^{23} = -45.6°$ *laevo*-menthol

It thus proved possible to interrelate the acidities of OH, CH, and NH acids, and to construct a general scale covering acids from methanol to cumene. McEwen adopted the value $pK_a = 16$ [59] for methanol, and on this basis determined values for weaker acids. He noted that his values were minima, because of the postulates made in the colorimetric determinations. Table 6 gives McEwen's scale, which remained the only one for a long time.

In 1959 Streitwieser et al. began to elaborate another scale of equilibrium acidity[60,61], also based on transmetallations. He measured the equilibrium constant between lithium or caesium cyclohexylamide and the CH acids, or between the lithium and caesium salts of the CH acids and cyclohexylamine, with cyclohexylamine as solvent:

$$RH + \text{cyclo-}C_6H_{11}\overset{\delta-}{N}H\overset{\delta+}{M} \rightleftharpoons \overset{\delta-}{R}\overset{\delta+}{M} + \text{cyclo-}C_6H_{11}NH_2\,. \quad (5)$$

In order that equilibrium transmetallation data can be used without correction as a measure of relative acidities, the organometallic compounds should correspond as closely as possible to the free carbanion. Streitwieser et al.[61,62] adduce the following arguments indicating that this condition is satisfied for the lithium and caesium salts of polyarylmethanes in cyclohexylamine.

Firstly, the salts absorb at far longer wavelengths than do the corresponding hydrocarbons: i.e. conjugation increases on passing to the salt. Secondly, solutions of most of these salts obey the Lambert–Beer law over a wide concentration range. Thirdly, a diminution in the polarity of the solvent is accompanied by a hypsochromic shift in the spectra (by 30–70 nm), probably due to breakdown of the solvation of the cation in the ion-pair[62]. The most significant aspect, however, is that, despite the sharp difference between lithium and caesium cations in electronegativity and ionic radius, the spectra are almost independent of the nature of the cation. The electrical conductivity of fluorenyl-lithium in cyclohexylamine is very close to that of lithium perchlorate in this solvent[63].

Table 6. McEwen acidity scale.

Compound	pK_a	Compound	pK_a
Methanol (standard)	16	Diphenylamine	23
Pyrrole	16.5	Fluorene	25
Benzyl alcohol	18	Aniline	27
Ethanol	18	*p*-Toluidine	27
Diphenylmethanol	18	*p*-Anisidine	28
Propan-2-ol	18	Xanthen	29
Triphenylmethanol	19	9-Phenylxanthen	29
t-Butyl alcohol	19	Biphenylyldiphenylmethane	31
t-Pentyl alcohol	19	Triphenylmethane	33
Methol	19	1-Naphthyldiphenylmethane	34
Acetophenone	19	Diphenylmethane	35
9-Phenylfluorene	21	1,1-Diphenylethane	36
9-1'-Naphthylfluorene	21	Cumene	37
Phenylacetylene	21		
Indene	21		

The spectral data obtained by Streitwieser et al. will be found in Ref. 60. On the basis of these results they assumed that lithium and caesium salts exist as ion-pairs in cyclohexylamine, and that interaction leading to the formation of a covalent bond could be neglected. In such case equilibrium constants (Eqn. 5) determined spectroscopically are an absolute measure of the difference in acidity[60]. These constants were linked with the pK_a values by relating them to the arbitrary standard 9-phenylfluorene (in aqueous sulpholan $pK_a = 18.5 \pm 0.1$ [64])§. The values obtained by Streitwieser et al. are listed in Table 7.

Table 7. Streitwieser acidity scale.

Compound	pK_a	Compound	pK_a
9-Phenylfuorene	(18.5)	1,1,3-Triphenylpropene	26.4
3,4-Benzofluorene	19.4	Dihydro-9,9-dimethyl-10-phenylanthracene	28.0
1,2-Benzofluorene	20.0	*p*-Biphenylyldiphenylmethane	30.2
4,5-Methylenefluorene	22.6	Triphenylmethane	31.5
Fluorene	22.8	Diphenylmethane	33.1
2,3-Benzofluorene	23.2		

The Streitwieser scale is more precise than the McEwen scale by an order of magnitude, but it covers a narrower class of hydrocarbons, being restricted to polyarylmethanes and structurally similar compounds. Comparison of Tables 6 and 7 shows that polyarylmethanes have almost the same affinity in ether, benzene, and cyclohexylamine: i.e. solvation factors have only a slight effect

§ Choice of this compound as standard may not be altogether correct, since in dimethyl sulphoxide 9-phenylfluorene has $pK_a = 16.4$ (Table 12).

on the pK_a in these solvents. Both scales have the disadvantage of not extending to very weak CH acids, including monoarylmethanes, alkenes, arenes, and alkanes. The two scales can be used to assess the acidity of methine acids having $pK_a < 33$ (on the Streitwieser scale).

Filler and Wang used Streitwieser's system (cyclohexylamine + lithium cyclohexylamide) to determine the equilibrium acidity of polyfluorinated tri- and di-phenylmethanes and several other compounds[65]. The results are given in Table 8.

Table 8. Equilibrium acidity of polyfluorinated aromatic compounds on the Streitwieser scale[65].

Compound	pK_a
$(C_6F_5)_3CH$	15.8
$(C_6F_5)_2CH_2$	21.3
$(p\text{-}CH_3C_6F_4)_3CH$	17.9
$(p\text{-}CH_3OC_6H_4)_3CH$	19.3
$(C_6F_5)_2CHCH(C_6F_5)_2$	22.7

Shatenshtein et al.[66,67] used the Streitwieser and McEwen scales to assess the acidities of derivatives of *o*-, *m*-, and *p*-carboranes in various solvents (ether, dimethoxyethane, and cyclohexylamine). The pK_a values obtained for these methine acids varied little with the nature of the solvent. Table 9 gives the acidities of carboranes in dimethoxyethane on the Streitwieser scale.

Table 9. Equilibrium acidity of carboranes in dimethoxyethane with potassium fluorenylide[a] as base at 25°C.

Compound	pK_a	Compound	pK_a
9,10-Dichloro-1,2-carborane	16.3[b]	1-Phenyl-1,7-carborane	27.5[c]
1-Phenyl-1,2-carborane	22.6	1-Methyl-1,7-carborane	27.9[c]
1-Methyl-1,2-carborane	23.1	*m*-Carborane	27.9[c]
o-Carborane	23.3	*p*-Carborane	30.0[c,d]
1-Isopropyl-1,2-carborane	23.9		

[a] Use of lithium fluorenylide gives pK_a values 1–2 units smaller than those in the Table.

[b] Lithium fluorenylide as base.

[c] Potassium 9-phenylxanthylide as base.

[d] In cyclohexylamine $pK_a = 31.0$.

Transfer from dimethoxyethane to ether as solvent has hardly any effect on the acidity of carboranes[68]. A wider range of ethereal solvents has been studied for the acid ionisation of 9,10-dihydroanthracene ($pK_a = 30.4$ on the Streitwieser scale) and biphenylyldiphenylmethane[69]. Values of pK_a for these two hydrocarbons in diglyme, dimethoxyethane, diethoxyethane, ether, and cyclohexylamine vary within the range $\Delta pK_a = 0.5$. Shatenshtein et al. have also determined the acidity of potassium nido-(3)-1,2-dicarbaundecaborate[70]. Hydrogen attached to five atoms (three boron atoms and two carbon atoms) in the pentagonal plane of a truncated icosahedron probably possesses acidic mobility.

$$B_9C_2H_{13}^-K^+ + A^-K^+ \rightleftharpoons B_9C_2H_{11}^{2-}K_2^+ + HA$$

(where HA represents fluorene or indene). On the Streitwieser scale this compound has $pK_a = 21.3$: i.e. it is a fairly strong CH acid, in spite of the presence of an integral negative charge.

Although the McEwen and Streitwieser acidity scales have found wide practical application, they nevertheless have the above defect of not extending to such hydrocarbons as monoarylalkanes, arenes, alkenes, and alkanes. This is solely because of experimental difficulties in determining the ionisation equilibrium positions of these hydrocarbons. Indirect methods of estimating the acidities of very weak CH acids are therefore attracting attention. The first attempt to set up a universal acidity scale for CH acids, covering all classes of hydrocarbons, was made by Cram[2], who used McEwen's and Streitwieser's transmetallation equilibrium data, together with original investigations by Dessy et al. and by Applequist and O'Brien, which will be discussed below.

2. Cram's MSAD Scale

The direct determination of the ionisation equilibrium of alkanes, alkenes, and other weak CH acids encounters serious experimental difficulties. A method for solving this problem was suggested by Applequist and O'Brien[71], who measured the equilibrium constants between iodobenzene and various lithium alkyls, alkenyls, aryls, and aralkyls in ether and in ether–pentane mixtures at −70°C. Table 10 lists the negative logarithms of the constants K_{Ap} for the equilibrium

$$RLi + PhI \overset{K_{Ap}}{\rightleftharpoons} RI + PhLi\,.$$

Table 10. Logarithms of equilibrium constants between iodobenzene and RLi and between diphenylmercury and R_2Mg (K_{Ap} and K_{De} respectively—see text).

R	$\lg K_{Ap}$	$\lg K_{De}$	R	$\lg K_{Ap}$	$\lg K_{De}$
cyclo-C_5H_9	6.90	—	CH_3	—	2
cyclo-C_4H_7	6.14	—	cyclo-C_3H_5	0.98	0.9
neo-C_5H_{11}	5.46	—	C_6H_5	0	0
iso-C_4H_9	4.59	—	$CH{=}CH_2$	−2.41	0.5
iso-C_3H_7	—	6	$CH_3CH{=}CH_2$	—	−0.2
n-C_3H_7	3.88	—	$CH_2C_6H_5$	—	−0.4
C_2H_5	3.50	4			

Another method for assessing the equilibrium acidity of very weak CH acids was proposed by Dessy et al.[72,73], who estimated the constants K_{De} of the equilibrium

$$R{-}Hg{-} + Ph'{-}Mg{-} \overset{K_{De}}{\rightleftharpoons} R'{-}Hg{-} + R{-}Mg{-}$$

between various dialkyl-, dialkenyl-, and diaryl-magnesium compounds and diphenylmercury in oxolan at 25°C. Table 10 includes the relative logarithms of the equilibrium constants for this reaction.

The data obtained by Applequist and by Dessy were used by Cram[2] to determine the relative stability of anions formed from very weak CH acids. Cram felt, in his own words, "inner consistency" (Ref. 2, p. 29) between these

workers' results and certain data on the kinetic acidity of alkanes. Making a rational approach to these data, he set up the first universal acidity scale, covering such weak acids as saturated hydrocarbons. Cram's scale, which he termed the MSAD (McEwen–Streitwieser–Applequist–Dessy) scale, is given in Table 11. As already noted, the Applequist and Dessy data show good mutual agreement with the exception of the values for the vinyl group. According to Dessy ethylene is more acidic, but according to Applequist benzene (Table 10). Preference was given to the Dessy scale in setting up the MSAD scale.

Table 11. Cram's MSAD scale[2].

Methine acid	pK_a	Methine acid	pK_a
Fluoradene	11	Ethylene	36.5
Cyclopentadiene	15	Benzene	37
9-Phenylfluorene	18.5	Cumene (α)	37
Indene	18.5	Triptycene (α)	38
Phenylacetylene	18.5	Cyclopropane	39
Fluorene	22.9	Methane	40
Acetylene	25	Ethane	42
1,3,3-Triphenylpropene	26.5	Cyclobutane	43
Triphenylmethane	32.5	Neopentane	44
Propene (α)	35.5	Propane (s-)	44
Toluene (α)	35	Cyclopentane	44
Cycloheptatriene	36	Cyclohexane	45

Cram's MSAD scale undoubtedly requires refinement, especially in the region of the alkanes. It gives for methane $pK_a = 40$; the same value had been suggested in 1944 by Morton[48], and later by Pearson and Dillon[29]. However, the value for methane on Kosower's scale[74] is 47. Furthermore, calculation based on the equation[75,76]

$$pK_{CH_4} - pK_{NH_4^+} = pK_{NH_3} - pK_{OH_3^+}$$

with $pK_{NH_3} = 35$ [76] yields $pK_{CH_4} = 58$. On the polarographic scale the value for methane is 57 (see below). Maksič and Eckert-Maksič calculated pK_a values for several CH acids from the degree of *s*-character of the carbon–hydrogen bond undergoing ionisation; their scale has the value 50 for methane[77]. Streitwieser suggested that, in the case of planar unsaturated hydrocarbons, the equilibrium acidity is proportional to the difference between the energies of delocalisation of π-electrons in the carbanion and in the initial hydrocarbon $E_{\pi A^-}$ and $E_{\pi AH}$.[78] Assuming that the resonance integral β (in the molecular-orbital method) remains constant on passing from one system to another, and disregarding the difference in solvation and change in bond angles on passing from the hydrocarbon to the carbanion, we can use the equation

$$\Delta E_\pi = E_{\pi A^-} - E_{\pi AH} = 2\alpha + \Delta M\beta$$

(where α is the Coulombic integral in the molecular-orbital method) to calculate the parameter ΔM, and hence values of pK_a for planar hydrocarbons using the equation

$$pK_a = a + b\Delta M .$$

The dependence of ΔM on pK_a for toluene, fluorene, and indene is a straight line on the McEwen scale. The resulting graph gives $a = 48$ and $b = -15.5$. The former can be regarded as the pK_a of methane, since all these hydrocarbons are derivatives of methane, for which $\Delta M = 0$.

Thus the MSAD scale gives minimum pK_a values for the alkanes, and their true equilibrium acidities are probably smaller by factors of $\sim 10^{10}$. Ritchie[79] reached a similar conclusion by a different line of reasoning—from the difference in the solvation of anions having delocalised and non-delocalised charges.

3. Equilibrium Acidity of CH Acids in Dimethyl Sulphoxide

In contrast to many other dipolar aprotic solvents, dimethyl sulphoxide remains unchanged on treatment with its conjugate base (the dimsyl anion $CH_3SOCH_2^-$).[80] Kolthoff and Reddy showed that a glass electrode can be used for titration in pure dimethyl sulphoxide[81], and that acid ionisation constants up to $pK_a \simeq 30$ can be determined potentiometrically. For dimethyl sulphoxide itself the value is 33.1.[82,83]

Table 12. Acidity of CH acids in dimethyl sulphoxide, water, and cyclohexylamine[83].

No.	Acid	pK_{dmso}	pK_{cha}	pK_{H_2O}
1	9-Cyanofluorene	8.4	—	14.2 (methanol)
2	1,3-Difluorenylpropane	8.7	—	—
3	Methyl fluorene-9-carboxylate	10.3	—	12.9*
4	Fluoradene	10.5	—	17 (methanol)
5	Malonitrile	11.0	—	11.1
6	Benzoylacetone	12.1	—	9.6
7	Tri-*p*-nitrophenylmethane	12.2	—	14.3*
8	Hydrogen cyanide	12.9	—	9.1
9	Pentane-2,4-dione	13.4	—	9.0
10	Nitromethane	15.9 16.9[85]	—	10.2
11	9-Phenylfluoroene	16.4	(16.4)	18.2*
12	Indene	18.5	17.8	18.2*
13	1,2-Benzofluorene	17.9	17.9	—
14	9-Methylfluorene	19.7	20.6	—
15	4,5-Methylenephenanthrene	20.0	20.5	—
16	Fluorene	20.5	20.6	21.0*
17	Benzyl cyanide**	21.3[86]	—	—
18	1,1,3-Triphenylpropene	23.1	24.5	—
19	9-Phenylxanthen	25.5	26.4	—
20	*p*-Biphenylyldiphenylmethane	26.9	28.1	—
21	Methyl phenyl sulphone	27[87]	—	—
22	Triphenylmethane	28.3	29.4	~34 (methanol)
23	Diphenylmethane	30.0	31.0	—
24	Dimethyl sulphoxide	33.1	—	—
	Acidity of alcohols			
	Methanol	27.0	—	18.3 (methanol)
	Ethanol	27.4	—	20.4 (ethanol)
	Propan-1-ol	28.0	—	—
	t-Butyl alcohol	29.2	—	—
	Water	29	—	—

* Values of p*K* measured with respect to the acidity function and related to the standard state in aqueous solution.

** In dimethyl sulphoxide containing ~1% of water.

The first acidity scale in dimethyl sulphoxide, including CH and NH acids, whose acidity was determined by titration with potassium dimsylate in the presence of triphenylmethane as indicator (which gave a coloured anion), was proposed by Steiner and Gilbert[84]. This scale has since been modified by Ritchie[83] and by Ritchie and Uschold[82]. Table 12 gives the acidity scale in dimethyl sulphoxide.

It is interesting to compare the acidity of CH acids in dimethyl sulphoxide with their acidity in water (last column in Table 12). Benzoylacetone and tri-*p*-nitrophenylmethane have the same acidity in dimethyl sulphoxide, but in water these compounds exhibit a difference

ΔpK_a = 4.7: the acidity of benzoylacetone increases on passing from dimethyl sulphoxide to water, whereas that of tri-*p*-nitrophenylmethane decreases. Nitromethane and 9-phenylfluorene have similar pK_a values in dimethyl sulphoxide, but in water nitromethane is more acidic and 9-phenylfluorene less acidic. The acidity of malononitrile, fluorene, and indene remains almost unchanged on passing from aqueous solutions to solutions in dimethyl sulphoxide. The remaining CH acids in Table 12 can be divided into two groups: the first group comprises 9-cyano-, 9-methoxycarbonyl-, and 9-phenyl-fluorene derivatives, fluoradene, triphenylmethane, and trisnitrophenylmethane, which have lower pK_a values in dimethyl sulphoxide than in aqueous solution; the second group includes benzoylacetone, acetylacetone, hydrogen cyanide, and nitromethane, which are more acid in water than in dimethyl sulphoxide. The first group obviously contains CH acids that form anions with a delocalised charge, whereas CH acids of the second group yield anions having their negative charge localised on the heteroatom.

The above results are easily interpreted on the basis of Parker's theory[14], according to which the change in equilibrium constants and rate constants on passing from protic to dipolar aprotic solvents is attributable mainly to solvation of the anions. We have noted earlier that anions with a localised charge are well solvated by hydroxylated solvents. Dimethyl sulphoxide, in contrast, will well solvate strongly polarisable anions with a delocalised charge[14]. Thus the solvation of the latter anions will improve on passing from water to dimethyl sulphoxide, whereas that of anions having a localised charge will deteriorate. As a consequence, the acid ionisation equilibrium will shift to the right in the first case, and to the left in the second case. These arguments are valid, of course, provided that the difference in solvation of all other species involved in the ionisation equilibrium can be neglected.

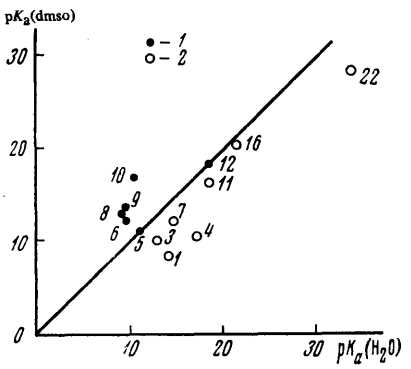


Figure 1. Dependence of acidity in dimethyl sulphoxide on acidity in water for carbanions: 1) well solvated by hydrogen bonds; 2) poorly solvated in water. Numbering as in Table 12. Straight line drawn at unit slope.

The relation between pK_a values in dimethyl sulphoxide and in water is plotted in Fig. 1 for several CH acids. The identity of pK_a values in water and in dimethyl sulphoxide for malononitrile and the other compounds located on the line of unit slope from the origin is fortuitous. With these compounds the energy of solvation of the anions of the conjugated bases changes little on passing from the solvent to water, although the actual nature of solvation becomes quite different. The fact that in water pentane-2, 4-dione is a stronger acid than malononitrile is due to stronger solvation of the conjugated base of the former by hydrogen bonds in water. In dimethyl sulphoxide the acidities of these two compounds have the "normal" sequence (Table 12). Thus the relative acidity in dimethyl sulphoxide corresponds more closely to the "true" acidity of the molecules (apparent in pure form in the gas phase—Section II)(than does the acidity in water.

The lower part of Table 12 gives pK_a values for water and simple alcohols determined in dimethyl sulphoxide. The acidity of alcohols in this solvent is evidently comparable with that of tri- and di-phenylmethane, which is consistent with qualitative results for ionisation in the gas phase (Section II) and diverges sharply from the "generally accepted" values of pK_a = 16—19 for alcohols[88]. This again is explained by a sharp decrease in basicity of oxygen-containing anions (increase in acidity of hydroxyl acids) in hydroxylated solvents due to hydrogen bonding. The high activity of metal alkoxides in dimethyl sulphoxide, first noted by Cram et al.[89], is now widely used in practical synthesis for accomplishing reactions in which the limiting or pre-equilibrium stage is detachment of a proton[2].

The penultimate column of Table 12 contains pK_a values for CH acids in cyclohexylamine. Here the value 16.4 has been chosen for 9-phenylfluorene[83], not 18.5 as in the Streitwieser scale. Hence the pK_a values for CH acids in cyclohexylamine given in Table 12 are smaller by 2.1 than the corresponding values on the Streitwieser scale. Transfer from dimethyl sulphoxide to cyclohexylamine is seen to have little effect on the relative acidities of the hydrocarbons.

4. Polarographic Acidity Scale

The polarographic method has the considerable merit of enabling acidities to be estimated over a very wide range of pK_a values in any polar solvent, even in one that is more "acidic" than the CH acid. It is based on the correlation between the cathodic reduction parameters of organomercury compounds having the general formula R_2Hg and the pK_a values of the corresponding acids RH

The first attempt to use polarography to assess the stability of carbanions was made by Streitwieser and Perrin[90], who measured the half-wave polarographic reduction potentials of substituted benzyl chlorides and polycyclic arylmethyl chlorides in dimethylformamide. If the transition state of this reduction

$$ArCH_2Cl + 2e^- \xrightarrow{E_{1/2}} ArCH_2^- + Cl^-$$

were structurally similar to the carbanion $ArCH_2^-$, a correlation could have been expected between the reduction potentials of the chlorides and the stabilities of the carbanions (i.e. the pK_a values of the methine acids). However, the slow stage in the reduction of halogenated organic derivatives in these systems proved to be transfer of the first electron, which is characterised by a radical-like transition state, so that the expected correlation was very poor. Dessy et al.[73] tried to use the half-wave potentials for the reduction of organomercury salts

$$RHgX \xrightarrow{\text{1st wave}} RHg \quad (\text{or } R_2Hg_2) \xrightarrow[\text{2nd wave}]{E_{1/2}} R^- + Hg$$

as a measure of the relative acidity of CH acids. However, this attempt also was unsuccessful.

The present Reviewers proposed determining the acidity of CH acids by measuring parameters of the cathodic reduction of symmetrical organomercury compounds

$$R_2Hg + 2e^- \xrightarrow{\alpha E_{1/2}} 2R^- + Hg\,.$$

This method takes into account not only the half-wave potential $E_{\frac{1}{2}}$ but also the change in the so called electrochemical transfer coefficient αn_a on passing from one organomercury compound to another[91,92]. On the assumption that the mechanism of cathodic reduction remains unchanged on passing from one mercury dialkyl to another over a quite large number of compounds, i.e. that only rupture of the carbon–mercury bond takes place in the transition state, with the group R acquiring a partial negative charge (which is probably true in most cases[93]), the tendency of the mercury dialkyl to undergo cathodic reduction can be related by simple reasoning with the acidity of the corresponding CH acid RH.

Three processes can probably be interrelated—(i) acid dissociation of the CH acid

$$RH \overset{K_a}{\rightleftharpoons} R^- + H^+\,, \qquad (6)$$

(ii) dissociation of the organomercury compound

$$R_2Hg \overset{1/K_m}{\rightleftharpoons} 2R^- + Hg^{2+}\,, \qquad (7)$$

and (iii) cathodic reduction of the organomercury compound

$$R_2Hg + 2e^- \rightarrow 2R^- + Hg\,.$$

The equilibrium constants (6) and (7) represent the stability of the carbanions in media containing a proton donor or a donor of the mercury cation respectively.

Deduction of a formula linking the acidity of CH acids with the cathodic reduction parameters of their mercury salts necessarily involved the assumption that the proton affinity of the carbanions was related linearly to their affinity for the mercury cation

$$\Delta \ln K_m = A \cdot \Delta pK_a \qquad (8)$$

(where A is a constant, $\Delta \ln K_m$ is the difference between the values of $\ln K_m$ for two organomercury compounds, and ΔpK_a is the difference between the pK_a values for the corresponding methine acids). The validity of this hypothesis has recently been proved[94] by analysing the nuclear magnetic resonance spectra of organomercury compounds. Scheffold has shown[95] that the spin–spin interaction constants between the magnetic isotope of mercury and the methyl protons $J_{^{199}Hg-CH_3}$ in complexes of the methyl mercury cation with various anions X^- (CH_3HgX) are proportional to the logarithm of the stability constants of these complexes:

$$CH_3Hg^+ + X^- \rightleftharpoons CH_3HgX;\ K_m' = \frac{[CH_3HgX]}{[CH_3Hg^+][X^-]}$$

Thus the (thermodynamic) stability of the bond between the cation CH_3Hg^+ and the anion of X^- can be assessed from the n.m.r. spectra. Scheffold's correlation embraces anions with various donor atoms—oxygen, sulphur, nitrogen, halogens, and, especially important, carbon (the cyanide anion)—and can be used to estimate the stability constants of complexes of the methylmercury cation with carbanions, in particular with alkyl anions.

Fig. 2 shows a plot of the constants $J_{^{199}Hg-CH_3}$ against $\lg K_m'$, representing the affinity of various anions X^- for the methylmercury cation. Values of $\lg K_m'$ for the anions—$CH\vdots C^-$, CF_3^-, $H_2C:CH^-$, CH_3^-, and C_2H_5—can be estimated by marking off on this graph points corresponding to compounds having low values of J (the sign of the constant remains unchanged throughout the series[96]).

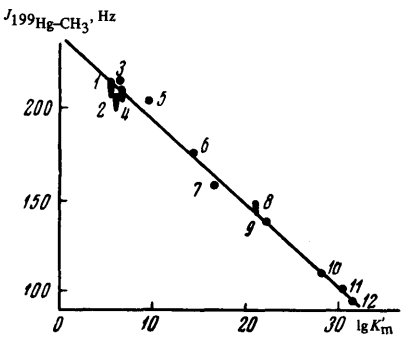


Figure 2. Linear relation between the constants $J_{^{199}Hg-CH_3}$ and $\lg K_m'$ for methylmercury compounds CH_3HgX, where X is: 1) Cl; 2) SCN; 3) $OCOCH_3$; 4) Br; 5) OH; 6) CN; 7) $SHgCH_3$; 8) $C\vdots CH$; 9) CF_3; 10) $CH:CH_2$; 11) CH_3; 12) C_2H_5.

The values obtained for $\lg K_m'$ (Table 13) correlate well with the pK_a values for the corresponding hydrocarbons on the Cram scale (Fig. 3). This relation is described by the equation

$$\lg K_m' = 0{,}6 \cdot pK_a + \text{const}\,.$$

Table 13. Affinity of carbanions for methylmercury cation.

No.	Anion	$\lg K_m'$	No.	Anion	$\lg K_m'$
1	CN^-	14.2	4	$CH_2{=}CH^-$	28
2	$HC{\equiv}C^-$	21	5	CH_3^-	30
3	CF_3^-	22	6	$C_2H_5^-$	31.5

By analogy with the above we can assume a linear relation also between the proton affinity of the carbanions and their affinity for the Hg^{2+} cation (Eqn. 8). For the equilibrium reduction of R_2Hg we have

$$\Delta G^0 = -RT \ln K_m + \Delta G_{Hg^0/Hg^{2+}}\,,$$

where the second term on the right-hand side is the redox potential of the Hg^0/Hg^{2+} system. Hence comparison of two organomercuric compounds yields

$$-\Delta\Delta G^0 = RT \cdot \Delta \ln K_m\,. \qquad (9)$$

From Eqns. (8) and (9) it follows that

$$-\Delta\Delta G^0 = RT \cdot A \cdot \Delta pK_a\,. \qquad (10)$$

Rates of reduction of organomercury compounds must be compared at the same potential E, at which each compound will be reduced with a certain overpotential

$$\eta = E - E^0, \tag{11}$$

where E^0 is the equilibrium potential for the given mercury dialkyl. From Eqns. (10) and (11) we obtain for the difference between the overpotentials of two organomercury compounds the formulae

$$\Delta\eta = -\Delta E^0;\ \Delta\eta = \frac{\Delta\Delta G^0}{F},\ \Delta\eta = A^* \cdot \Delta pK_a, \tag{12}$$

where A^* is a constant.

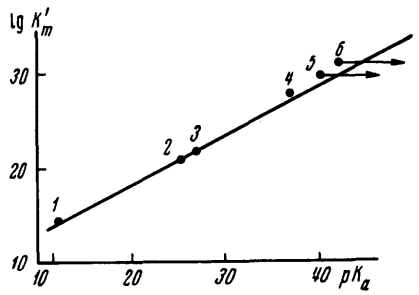


Figure 3. Relation between $\lg K'_m$ and pK_a on MSAD scale. Numbering of compounds as in Table 13.

The cathodic reduction rate constant depends on the overpotential[97]:

$$\ln k_e = \ln k_e^0 - \frac{\alpha n_a F}{RT}\eta, \tag{13}$$

where k_e^0 is the rate constant at the equilibrium potential, n_a the number of electrons involved in the slow stage, and α the electrochemical transfer coefficient¶. Equation (13) presupposes that the transfer coefficient α is independent of the overpotential. If α does depend on the overpotential[98,99], Eqn. (13) can be written, with $n_a = 1$,

$$\ln k_e = \ln k_e^0 - \frac{F}{RT}\int_0^{\eta} \alpha\, d\eta. \tag{14}$$

The difference between the rates for any pair of mercury dialkyls at the same potential, in particular at $E = 0$, is given by the formula

$$\Delta \ln k_e = \Delta \ln k_e^0 - \frac{F}{RT}\int_{\eta_1}^{\eta_2} \alpha\, d\eta.$$

whence

$$\Delta \ln k_e = \Delta \ln k_e^0 - \frac{\alpha_e F}{RT}\Delta\eta \tag{15}$$

in which α_e is the mean transfer coefficient over the range of overpotentials $\eta_1 - \eta_2$.

From Eqns. (12) and (15) we obtain

$$\Delta \ln k_e = \Delta \ln k_e^0 - \alpha_e \cdot A \cdot \Delta pK_a, \tag{16}$$

which shows that the relative rate of reduction of a mercury dialkyl at a given potential depends not only on the relative stability ΔpK_a of the corresponding carbanion R^- but also on the relative rate of reduction of the compound R_2Hg when $\Delta pK_a = 0$, i.e. on the difference between the rates of electron transfer at the equilibrium potentials $\Delta \ln k_e^0$. We may suppose by analogy that $\Delta\eta$ for electron transfer is equivalent to $\Delta pK_a = pK_a(HA) - pK_a(HB)$ for the proton transfer $HA + B^- \rightleftharpoons A^- + HB$, and $\Delta \ln k_e^0$ to the relative rate of proton transfer when $\Delta pK_a = 0$. The quantity $\Delta \ln k_e^0$ is evidently connected with the energy of structural reorganisation of the R_2Hg-R^- system involved in electron transfer. The change in rate of proton transfer when $\Delta pK_a = 0$ observed with change in the structure of the acid may be due to a change in the pK_a of the latter[13] Similarly, in the case of electron transfer we may suppose to a first approximation that $\Delta \ln k_e^0$ varies linearly with $\ln K_m(R_2Hg)$, i.e. with $pK_a(RH)$. If $\ln k_e$ is assumed to be constant over the given range of overpotentials, we find from Eqn. (16) that

$$\Delta \ln k_e = -\rho' \cdot \Delta pK_a \tag{17}$$

It thus remains to measure only the rate constants of cathodic reduction for a series of mercury dialkyls at the same potential, and the problem of determining the acidity of CH acids will be solved. However, since the organomercury compounds R_2Hg are reduced at potentials from 0 to −3 V depending on the nature of R, such measurements are impossible. We are therefore compelled to estimate the rate constants by means of the Koutecky–Delahay equation[100], which, provided that the drop period of the mercury electrode is constant and the diffusion coefficient of the mercury dialkyl varies little with the nature of the alkyl group, is written

$$\frac{\alpha n_a F}{RT} E_{1/2} = \ln k_{E=0} + \text{const}, \tag{18}$$

where $k_{E=0}$ is the rate constant of electron transfer at $E = 0$ relative to some reference electrode, and α is the polarographic transfer coefficient at the half-wave potential $E_{\frac{1}{2}}$. We find from Eqns. (17) and (18) that

$$\Delta(\alpha n_a E_{1/2}) = \rho \cdot \Delta pK_a, \tag{19}$$

where ρ is a constant depending on the experimental conditions. This constant cannot be calculated, and must therefore be determined experimentally each time.

Fig. 4 illustrates diagrammatically the dependence of $\ln k_e$ on the electrode potential[98,99]. The error in the determination of $\ln k_e$ obviously depends on the choice of potential E' at which the rates of reduction of the mercury dialkyls are compared. Thus the quantity $\alpha n_a E(E_{\frac{1}{2}} - E')/RT$, which is determined by linear extrapolation of the tangent at the point $E_{\frac{1}{2}}$ to the potential E' (Fig. 4), does not represent the true value k'_e, and the discrepancy will be larger when the compound is reduced at more negative potentials.

In spite of a number of theoretical limitations, Eqn. (19) was found to hold for a large number of organomercury

¶ This parameter has an analogous significance to the Brønsted coefficient for proton transfer. Change in potential corresponds to a change in equilibrium between oxidised and reduced forms of the substance, just as a change in pK_a corresponds to a change in the position of protolytic equilibrium. The quantity α shows the extent to which potential influences the rate of the forward reaction. The value of αn_a is readily determined from the slope of the polarograms.

compounds corresponding to a series of CH acids with a range of variation in pK_a exceeding 50.[101-107] In this way a polarographic acidity scale was set up, which included CH acids having pK_a values of 7–60 (Table 14).

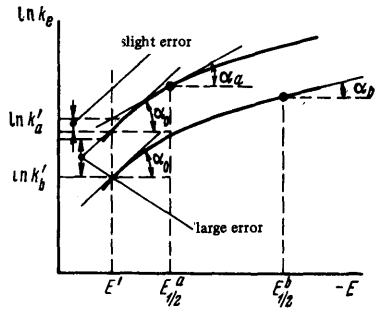


Figure 4. Scheme illustrating dependence of $\ln k_e$ on electrode potential for two different compounds R_2Hg.

Anhydrous dimethylformamide was used as solvent for the polarographic measurements. Half-wave potentials and αn_a were evaluated by means of Heyrovský graphs, and the dependence of the product $\alpha n_a E_{\frac{1}{2}}$ on the pK_a values of the corresponding CH acids was then plotted (Fig. 5).

Table 14. Polarographic acidity scale for CH acids.

Acid	Position of CH bond	pK_a	Acid	Position of CH bond	pK_a
Propane	2	60	Fluoroform		26
Methane		57	Methyl phenyl sulphone	α	25
1,3,5-Trimethylpyrazole	4	38	Ethyl difluoroacetate	α	25
Indole	3	38	Methyl acetate	α	24
	2	35	Pentafluorobenzene		23
Ethylene		37	1,1,1,2,3,3,3-Heptafluoro-		
Benzene		37	propane	2	22
Furan	3	37	1,1,1,3,3,3-Hexafluoro-		
	2	36	propane	2	22
2-Methylbenzofuran	3	36	*m*-Carborane	1 or 7	22
3-Methylbenzofuran	2	35	Ethyl fluoroacetate	α	22
2-Methylbenzothiophen	3	36	t-Butyl methyl ketone	$COCH_3$	21
3-Methylbenzothiophen	2	35	Trifluoroethylene		20
Toluene	α	35	Ethyl chlorofluoroacetate	α	20
Thiophen	2	35	Phenylacetylene		19
Selenophen	2	35	*o*-Carborane	1 or 2	18
1-Acetylindole	3	34	Cyclopentadiene	CH_2	16
1-Acetyl-3-methylindole	2	33	Chloroform		15
3-Acetyl-1-methylindole	2	32	Ethyl ββ-trifluoropropionate	α	15
p-Carborane	1 or 12	32	Ethyl αββ-tetrafluoro-		
Pentachlorobenzene		31	propionate	α	14
Vinyl chloride	2	31	Ethyl bistrifluoromethyl-		
			acetate	α	13
			Hydrogen cyanide		12
			Bromoform		9
			Tristrifluoromethyl methane		7

The following CH acids were chosen for the experimental determination of the constant ρ (Eqn. 19)—(i) hydrogen cyanide, with pK_a = 12 determined by potentiometric titration in dimethylformamide, (ii) phenylacetylene, cyclopentadiene, toluene, and benzene, whose acidities were known on the MSAD scale, and (iii) methyl acetate, whose pK_a was taken to be 24 [104]—and a calibration graph was drawn through these points. Knowing the values of αn_a and $E_{\frac{1}{2}}$ for other organomercury compounds, we can hence determine the pK_a values for other CH acids. The graph in Fig. 5 shows that a correlation actually exists between values of $\alpha n_a E_{\frac{1}{2}}$ for R_2Hg and the pK_a of the corresponding acids RH.

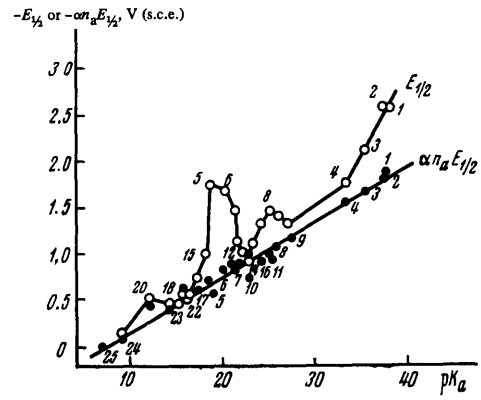


Figure 5. Correlation of parameters of polarographic reduction of organomercury compounds with acidity of corresponding CH acids. Numbering of points corresponds to that of compounds in Table 1 of Ref. 93.

It is important to note that the half-wave potentials do not correlate with the acidity. The reason is that they do not have the same physical significance in an irreversible electrochemical process as in reversible reduction: i.e. the value of $E_{\frac{1}{2}}$ does not directly represent the redox properties of the substance that is reduced irreversibly.

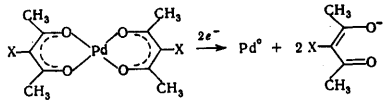
The polarographic method enabled a very wide range of variation in acidity to be investigated. It can be used to determine the acidity of compounds containing groups sensitive to the action of bases and, what is very important, the relative stability of isomeric carbanions differing in the position of their charge. The main experimental difficulty (usually easily overcome) is the need to prepare isomeric mercury derivatives of the CH acids.

The correlation of $\alpha n_a E_{\frac{1}{2}}$ with pK_a is valid only when the carbon–mercury bond alone is broken in the transition state, and no subsequent processes stabilising the resulting carbanion influence the potential. This requirement may not always be made for compounds towards the end of Table 14, since their reduction is in considerable measure reversible: e.g.

$$(CBr_3)_2Hg \overset{2e^-}{\rightleftharpoons} Hg + 2CBr_3^- \xrightarrow[\text{potential}]{\text{influences}} 2\,CBr_3 + 2Br^-.$$

If the proton affinity of carbanions is assumed to be linearly related to their affinity not only for the mercury cation but also for cations of other metals, similar correlations between cathodic reduction parameters and pK_a values should be observed for many other organometallic compounds. We have examined published data[108,109], and found that Eqn. (19) holds for acetylacetonate complexes of

palladium and acidopenta-amminecobalt complexes, which are reduced according to the schemes



$$[Co(NH_3)_5X]^{n+} \xrightarrow{e^-} [Co(NH_3)_5]^{n+} + X^-$$

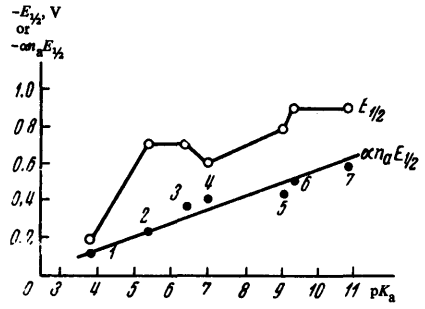


Figure 6. Dependence of $\alpha n_a E_{\frac{1}{2}}$ on pK_a of substituted acetylacetones for acetylacetonate complexes of palladium (substituent X): 1) CN; 2) $NHCOCH_3$; 3) $COOC_2H_5$; 4) Br; 5) H; 6) C_6H_5; 7) CH_3.

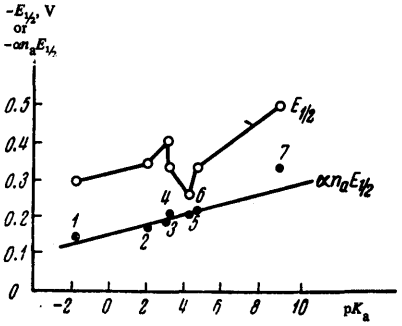


Figure 7. Dependence of $\alpha n_a E_{\frac{1}{2}}$ on pK_a of HX for reduction of $[CoX(NH_3)_5]$ where X is: 1) H_2O; 2) HSO_4^-; 3) F^-; 4) NO_2; 5) fumarate; 6) CH_3COO^-; 7) NH_3.

Figs. 6 and 7 show that the product $\alpha n_a E_{\frac{1}{2}}$ for the palladium complexes correlates well with the pK_a values of the corresponding pentane-2,4-diones, and that for the cobalt complexes with the pK_a values of the acids HX. As with the organomercury compounds, a linear relation is not observed between pK_a and $E_{\frac{1}{2}}$ (Figs. 6 and 7). With reversibly reducible cobalt complexes containing a cobalt–carbon σ-bond, however, good correlations are observed between the half-wave potential of the first polarographic wave and the pK_a values of the corresponding carbanions[110]. Graphs illustrating this relation are given in Figs. 8 and 9.

5. Breslow's Electrochemical Method

An interesting electrochemical method for determining the acidity of hydrocarbons for which direct measurement of pK_a is impossible was suggested by Breslow et al.[111-113]. It involved indirect determination of equilibrium acidity on the basis of the series of reversible reactions

$$R{-}H \overset{1}{\rightleftharpoons} R{-}OH \overset{2}{\rightleftharpoons} R^+ \overset{3}{\rightleftharpoons} R\cdot \overset{4}{\rightleftharpoons} R^-.$$

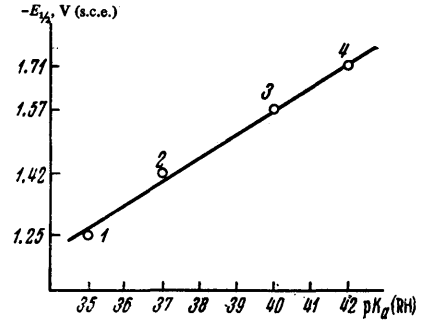


Figure 8. Dependence of half-wave potential for reduction of the complexes [CoR salen dmf] complexes[109] (first wave) on pK_a of RH on MSAD scale for R: 1) $C_6H_5CH_2$; 2) C_6H_5; 3) CH_3; 4) C_2H_5.

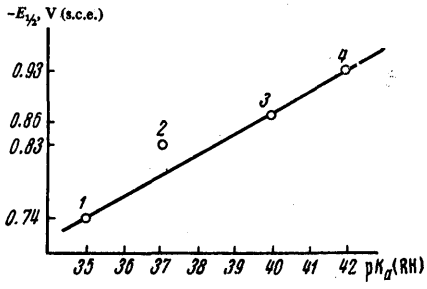


Figure 9. Dependence of half-wave potential for reduction of [CoR(DO)(DOH)pn dmf] [109] on pK_a(RH). Numbering as in Fig. 8.

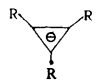
Breslow's method is applicable to hydrocarbons which yield relatively stable carbonium ions and relatively unstable carbanions. In this case it is easy to determine thermodynamic parameters for stages *3* and *4* by some electrochemical method, e.g. by measuring the redox potentials for the reduction in stages of the carbonium ion to the carbanion. The thermodynamic parameters for stage *2* are Deno's pK_{R^+} values[114], which characterise the equilibrium

$$R{-}OH + H^+ \overset{K_{R^+}}{\rightleftharpoons} R^+ + H_2O$$

between the alcohol and the carbonium ion. It is difficult to obtain thermodynamic parameters for stage *1*, but it was suggested that the difference between the heats of formation of hydrocarbon and alcohol was roughly constant for a series of related compounds.

Breslow et al. took $pK_a = 33$ on the McEwen scale for triphenylmethane as basis, and determined the thermodynamic acidity of several substituted triphenylmethanes,

as well as cycloheptatriene and substituted cyclopropenes (Table 15). The high pK_a values for substituted cyclopropenes are explained by the instability (anti-aromaticity) of the corresponding anion



unstable

Breslow's method is primarily valuable because such a low acidity is difficult to investigate by other methods.

Table 15. Breslow acidity scale for CH acids[111-114].

pp'p"-Trisubstituted triphenylmethane	pK_a ±2,0	Compound	pK_a
Trichloro	32,3	Cycloheptatriene	36±3
Monomethoxy	33,1	Triphenylcyclopropene	51±4
Trimethoxy	33,4	Trimethylcyclopropene	62±5
Trisdimethylamino	34,7	Tri-n-propylcyclopropene	64±5
Trimethyl	33,6	Tri-t-butylcyclopropene	65±5
Tri-isopropyl	36,2		
Tri-t-butyl	35,2		

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In this Review we have been considering only papers reporting the determination of the equilibrium acidity of a *series* of CH acids by various methods, i.e. in which scales of relative acidity have been set up. There are also many isolated data on the acidity of individual CH acids, determined under various conditions (e.g. in an alkali-metal alkoxide—alcohol system) or estimated indirectly. These results, which undoubtedly merit attention, have been excluded from the present paper to avoid increasing its length.

It is now possible to determine the acidity of CH acids in aprotic solvents up to values of $pK_a \simeq 30$. The acidity of weaker acids (alkenes, arenes, alkanes, etc.) is assessed by indirect methods, since no direct methods are available. The acidity of these compounds is evidently less than that predicted by Cram's MSAD scale. The main problem of future research will be to compile a *quantitative* scale of acidities in the gas phase and to work out methods for calculating theoretically the empirical constants occurring in the equations relating pK_a values with other thermodynamic or kinetic parameters.

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