

CH- ACIDS

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Translation Editor: T. R. Crompton

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A guide to all existing problems of CH-acidity with
new experimental methods and data, including indirect
electrochemical, kinetic and thermodynamic studies

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CH-ACIDS

**A guide to all existing problems of CH-acidity with
new experimental methods and data, including indirect
electrochemical, kinetic and thermodynamic studies**

Preface

Almost all organic compounds are CH-acids because they contain C-H bonds the hydrogens of which are capable of being substituted by metals resulting in carbon-metal bonds. In other words, organometallic compounds are salts of CH-acids and the properties of CH-acids belong in the domain of organometallic chemistry. The authors have been working in this field for many years and this book is indeed addressed to organometallic and organic chemists. This does not necessarily mean that the authors wish to single out a particular audience; in fact, their aim is to explain their special interest in, for instance, proton transfer stereochemistry or structure vs. CH-acidity patterns. On the other hand, although there is a very direct relation between organometallic reactivity and CH-acidity, this problem is not treated in this book since this aspect of the problem of reactivity will already be well known to organometallic chemists.

The present book deals with the acidity proper, not with carbanion chemistry nor organometallic chemistry. Not all aspects of carbanion chemistry or organometallic chemistry pertain to CH-acidity, but both of the problems have much in common.

CH-acidity characterises thermodynamic stability of carbanions in a medium containing a proton donor as carbanion acceptor. Many other acceptors may be employed for the purpose, e.g. Hg^+ , Ag^+ , RHg^+ , and other, cations. However, proton donors are the most convenient to deal with since, firstly carbanion affinity for the proton was the easiest to determine experimentally and, secondly, the data obtained are comparable with a wealth of data available on OH- and NH-acidities and, thus, the stability of carbanions may be collated with the stability of O-, H-, and other anions in various solvents and in the gas phase.

A problem currently being worked on is the experimental determination of acidity in the gas phase, which would make it possible to construe a quantitative intrinsic acidity scale not influenced by solvent. The first results of this work have already been obtained using the ion cyclotron resonance method (to be discussed in Chapters I and II). The acidity series in the gas phase has been found to be quite different from that obtained in solution.

Acidity in solution is of special importance because organic chemistry is, in the main, the chemistry of solutions. Dimethyl sulphoxide, liquid ammonia, cyclohexylamine, and some other solvents are excellent for a study of CH-acidity and it is in these solvents that most data on equilibrium and kinetical acidities has been obtained. However, pK_a values found in cyclohexylamine correspond to ion-paired rather than dissociative acidity; O-bases in dimethylsulphoxide are ion-pairs of alkali cations and this also affects pK_a 's of CH-acids measured in a dimethylsulphoxide/O-based system.

On the whole, the effects of ion-pair formation upon equilibrium CH-acidity have not been exhaustively studied and, in this direction, there is still much to be done, especially on the theoretical level.

The first two chapters of the book discuss equilibrium CH-acidity. Chapter I describes methods to study equilibrium acidity and the pKa values of numerous CH-acids are tabulated. The determination of the acidity of weak acids such as CH-acids lead to difficult experimental problems which are concerned with a large pKa scale depending on CH-acid structures. An important task, therefore, is a search for new direct or indirect approaches to determining relative acidities. Recently, a great amount of published work has appeared in this field and this is discussed in Chapter I. It should be noted that for the most part the methods available may be applied only in a rather narrow pKa interval whereas the problem of creating a general-purpose method capable of giving the pKa of any acids with a wider pKa interval still awaits solution. Chapter II discusses equilibrium acidity as a function of CH-acid structures.

In Chapter III, the hydrogen isotope exchange in CH-acids, i.e. the so-called kinetic CH-acidity is discussed. Isotope exchange is discussed as a method of finding the relative reactivity of C-H bonds in a series of CH-acids studied in one and the same solvent base system.

Chapter IV is devoted to the stereochemistry of proton transfer in CH-acids. Proton transfer from tetrahedral carbon atom allows one to understand better the nature of transition states and the role played by ion-pairing and solvation. Stereochemical problems are specific to CH-acids; they do not arise when studying acids of other types and in this aspect there is a significant difference between CH-acids and OH- or NH-acids. The stereochemical aspect is an essentially new aspect contributed by CH-acids in a study of acidity on the whole.

Equilibrium vs. kinetic acidity is discussed in Chapter V. The authors believe that the Brønsted equation is a fundamental law but there are numerous factors obscuring experimental observation of the action of this law. These factors are discussed extensively. Anomalous Brønsted slopes observed in some cases are explained by effects of the medium indicating again the importance of studies of rates and equilibria in the gas phase.

We are grateful to A.V.Grib (Cand. Chem. SC., NMR Laboratory, Department of Chemistry, Moscow University) who has translated the Russian manuscript into English.

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Chapter I

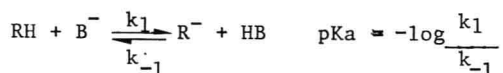
Equilibrium Acidity of CH-Acids

I. INTRODUCTION

Almost any organic compound can, when acted upon by a base (a proton acceptor) of appropriate strength, ionise in solution to give carbanions, that is, negatively charged species whose charge is totally or (more often) partially localised on one of the carbon atoms. This property of CH-bonds gives rise to a great variety of organic reactions in which proton abstraction is a limiting or a pre-equilibrium step. Some examples are carbonyl-methylene condensations, trans-metalation reactions, the allyl rearrangement, cyclisation/recyclisation rearrangements, etc.

Shatenshtein¹ was the first to consider hydrocarbons in terms of the general theory of acids and bases. The recent decade has brought a number of surveys of CH-acidity^{2,5}, among which the monograph by Cram² may be mentioned.

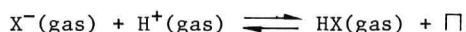
It is proposed to use the term "acidity" instead of the alternative "acid ionisation constant", in order to emphasise the relation between the equilibrium (thermodynamical) acidity (acid ionisation constant, K_a)



and the kinetic acidity (k_1), the rate of proton abstraction from the acid molecule. The equilibrium and kinetic acidities, i.e. the quantities pK_a and $\log k_1$, often vary in parallel.

To begin with, consider equilibrium CH-acidity. It does not depend on a proton abstraction mechanism and is the best characteristic of the thermodynamical stability of carbanions in a given system. In solution, the energy of any species participating in the acid-base equilibrium should be corrected for the solvation energy. It is advantageous therefore to consider first acid-base equilibria in the gas phase as this reflects the "intrinsic" CH-acidity and is not affected by solvation. Following this, this Chapter will deal with acid-base equilibria in solution.

The acidity of any acid in the gas phase may be written as⁶



where \square is affinity for proton.

The \square value is the enthalpy of proton addition to the anion and may be

represented in the following form,

$$\square = -\Delta H_{HX} + \Delta H_X^- + \Delta H_H^+$$

where ΔH_{HX} , ΔH_X^- , and ΔH_H^+ are the enthalpies of formation of HX, X^- and H^+ respectively. The heat of proton formation, $-\Delta H_H^+$, is the heat of the following reaction.



ΔH_{HX} can be found from experiments directly, while the heat of formation of anions in the gas phase may be obtained by, e.g., the Yatsimirskii⁷ method that assumes that the energy of a salt crystal lattice is the enthalpy of transformation of the solid salt to the ion gas consisting of the same ions

$$U_{KA} = -\Delta H_{KA}^O + \Delta H_K^O + \Delta H_A^O-$$

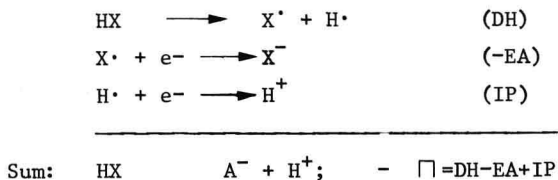
where $-\Delta H_{KA}^O$, $-\Delta H_K^O$, and $-\Delta H_A^O$ are the heats of formation of the crystalline salt, gaseous cation and gaseous anion, respectively. The crystal lattice energy is given by the Fayance equation.

$$U_{KA} = H_K^+ + H_A^- - L_{\text{solv}}.$$

where H_K and H_A are the heats of ion hydration and L_{solv} is the heat of solution of the salt at the ion strength of zero.

The data on the heats of formation and on crystal lattice energies allow one to calculate the energy of formation of ions in vacuo and the proton affinities of the anion, the latter not usually being obtainable by direct experiment.

The proton affinity may be found through the following thermodynamical sequence^{3,8}.



where DH is the X-H bond energy, EA is the affinity for electron of the radical X and IP the ionisation potential of hydrogen. Recently, Brauman⁸ and other workers⁹ using the ion cyclotron resonance technique have determined the affinity for the electron for a number of radicals and employed the thermodynamical sequence described above for calculating the values for a number of element hydrides. These data, together with the calculations performed using the method of Yatsimirskii⁷ are listed in Table 1.

TABLE 1
Proton Affinities for some Anions at Medium Vacuum 6-9

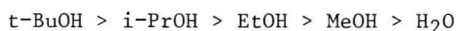
Anion	□ kcal/mole		Anion	□ kcal/mole	
	refs 6, 7	refs 8, 9		refs 6, 7	refs 8, 9
CH ₃ ⁻	-	-	HS ⁻	343	350
NH ₂ ⁻	419	407	CH ⁻	325	333
OH ⁻	383	390	NO ₃ ⁻	320	-
F ⁻	363	370	Br ⁻	315	324
PH ₂ ⁻	-	364	I ⁻	307	314
RCOO ⁻	about 350	-	HSO ₄ ⁻	296	-
CN ⁻	348	-	ClO ₄ ⁻	285	-

The data in Table 1 suggests that the acidity of hydrides in vacuo should rise in going from the left to the right in the Periodic System and downwards in each of the Groups.

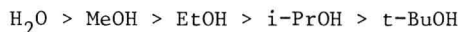
The data obtained may be summarised to give the series in which Brønsted acids are arranged in the order of the decrease in acidity at medium vacuum at 300°K, ^{9b}.

n-C₄H₉SH > CH₃NO₂ > cyclo-C₅H₆ > CHCl₃ > CH₃OOCH₃ > CH₃CN > CH₂Cl₂,
CH₃SOCH₃ ≥ C₂H₆, tert-C₄H₉OH, iso-C₄H₉OH > C₂H₅OH > CH₃OH > C₃H₄,
C₆H₅CH(CH₃)₂ > C₆H₅CH₃ > C₃H₆ > H₂O > C₆H₆ > H₂ > NH₃ > C₂H₄, C₆H₁₂
> (CH₂)₃, CH₄

This series is in dramatic contrast with the usual acidity concept based on studying aqueous and alcohol solutions of acids. Thus the alcohol acidity series in the gas phase ^{10,11}.



is the reverse of the series obtained in hydroxyl-containing solvents,



Consequently, the methyl group effect in the gas phase disagrees with the conventional (+I)-pattern. Brauman and Blair¹⁰ introduced an electrostatic model to explain the methyl-induced stabilisation of alkoxide ions. The model includes the interaction of charge with polarisable alkyl groups and predicts that an increase in the size of R in the group RO⁻ should lead to an increase in the R polarisability and to a decrease in the anion potential

energy ("inner solvation").

The R polarisability effect is not observed in hydroxyl-containing solvents because the energy of solvation ("outer solvation") of the negative oxygen with hydrogen bonds is markedly higher than is the energy of interaction of the ion spearhead with the dipole induced by it.

The weakest acid in the series discussed above is methane. The acidity rises, however, when one of the hydrogens is replaced by a group that may stabilise the carbanion. Thus the introduction into methane of an electron withdrawing chlorine atom may place the CH-bond value beneath the ammonia - Π value, $\text{CH}_3\text{Cl} > \text{NH}_3 > \text{CH}_4$, while toluene, whose phenyl group stabilises the negative charge via a conjugation mechanism, is a stronger acid than is water¹³. Accordingly, cumene in the gas phase is stronger than methane, i.e., alkyl groups do not obey the (+1)-pattern assumed for them conventionally.

The energies in Table 1 and the qualitative series given above, when collated, lead to the following acidity series in the gas phase.

$\text{HBr} > \text{RSH}, \text{H}_2\text{S} > \text{HCN} > \text{CHCl}_3 > \text{CH}_3\text{CN} \geq \text{HF}, \text{CH}_2\text{Cl}_2, \text{CH}_3\text{SOCH}_3 > \text{alcohols} > \text{C}_6\text{H}_5\text{CH}_3 > \text{H}_2\text{O} > \text{C}_6\text{H}_6 > \text{NH}_3 > \text{CH}_4$

The position of hydrogen fluoride in the series is due to the fact that fluorine ion in $\text{Et}_4\text{NF} \cdot 2\text{H}_2\text{O}$ can split a proton from, e.g., acetonitrile¹³.



The position of hydrogen fluoride agrees with the results published recently by McIver and Miller¹⁵⁸ whose data allow one to arrange alcohols, acetylenes, and hydrofluoric acid in the following series in the gas phase at 298°K.

$(\text{CH}_3)_3\text{CCH}_2\text{OH} > \text{HF} > \text{t-BuOH} > \text{i-PrOH} > \text{t-BuC} \equiv \text{CH} > \text{PrC} \equiv \text{CH} > \text{EtOH} > \text{CH}_3\text{C} \equiv \text{CH} > \text{MeOH}$

The series demonstrates that no distinction exists between CH-acids and acids of other types in the gas phase and all the types are arranged randomly. The same conclusion was reached by Ritchie and King¹⁴ who calculated the potential energy surfaces for simpler reactions involving the hydride ion attack along the X-H bond axis.



Water, ammonia, and methane were found to behave similarly, except that the energy differences between the reactants and the proton transfer products were different.

Consequently, hydrocarbons and their derivatives are not less efficient at displaying their acid properties than are hydrides and substituted hydrides of other elements. In this respect acetic acid may be regarded as an acetylated oxygen hydride (water).

In hydroxyl-containing solvents, however, the acid properties of hydrides and substituted hydrides of electronegative elements (e.g., OH-acids) are

much more pronounced than are CH-acidities. Hydroxyl-containing solvents favour the ionisation of OH-acids because they can form hydrogen bonds with electronegative elements. The next Section will compare CH- and OH-acidities in water.

II. CH-ACIDITIES IN WATER. A COMPARISON WITH HYDROXY ACIDS

Toluene in the gas phase is a markedly stronger acid than is water¹². It is profitable to consider whether in a hydroxyl-containing solvent toluene is a stronger or weaker acid than water¹⁵. The acid-based equilibria in these systems may be written in the following form.



To calculate dissociation or ionisation constants in solution, it is necessary to include the solvation of all the equilibrated species, both on the right and on the left hand side of the equations. When the proton acceptor, B, is one and the same and both reactions are made in the same solvent, then the calculation of relative acidities of water and toluene will deal only with the toluene and water solvation energies (on the left) and the hydroxyl and benzyl anion solvation energies (on the right).

The difference between solvation of water and toluene in hydroxyl-containing solvents is a result of the fact that the solvation is mainly due to hydrogen bonding. Eigen has grouped the following series as a measure of the ability to form hydrogen bonds¹⁶, OH...O > OH...N, NH...O > NH...N > SH...X, XH...S > PH...X, XH...P > CH...X, XH...C where X is any element.

It is clear from this tabulation that OH- and CH-acids lie at the opposite ends of the series; the former acids are the strongest, the latter ones the weakest hydrogen bond donors. Consequently, the water energy decreases more than does the toluene energy, on going from the gas phase to a hydroxyl-containing solvent such as water.

Similarly, O-bases are the strongest while C-bases are the weakest hydrogen bond acceptors, so the hydroxyl ion energy decreases more than does the benzyl anion energy on going from the gas phase to aqueous solutions.

Probably, the main effect on relative acidities of water and toluene in water is the anion solvation difference. Parker¹⁷ who studied reactions and equilibria in which anions participated showed that the solvent-induced increment in the anion solvations provides the most important contribution in the energy. The hydroxide ion, a small ion with a localised charge, is solvated with water very effectively whereas the benzyl anion whose charge is delocalised would have solvated less had it not been protonated instantaneously. This agrees with the hard and soft acids and bases principle introduced by Pearson¹⁸. As a result, the difference between the solvation energies of hydroxyl ion and water exceeds noticeably the difference between the solvation energies of toluene and the benzyl anion. In other words, a hydroxyl-containing solvent favours the $\text{H}_2\text{O} \rightarrow \text{OH}^-$ transformation much more than it does so with $\text{PhCH}_3 \rightarrow \text{PhCH}_2^-$. Therefore, the equilibrium in the water phase as compared with the gas phase is shifted to the right for water much more significantly than it is for toluene.(Table 2).

TABLE 2

Water and Toluene Acidities as a Function of Solvation
in changing from the Gas to the Liquid Water Phase¹⁵

Extent of solvation of an ion or a molecule		Total acidity increment
H ₂ O high	OH ⁻ very high	high
PhCH ₃ poor	(PhCH ₂ ⁻) (poor)	small*

* That is why the anion is "instantaneously" protonated in water.

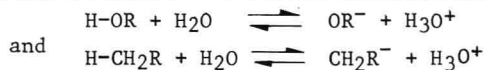
As a consequence of this, solvation effects in the aqueous phase appreciably increases the acidity of water, a weak acid in the gas phase, whereas toluene does not reveal its acid properties, that is, it remains as weak an acid as it was in the gas phase.

It can be concluded that the benzyl anion is a "strong base" although "strong base in water" would be more to the point since it has already been seen that both bases are strong in the gas phase.

This example shows why CH-acids in water are markedly weaker than are OH-acids. This is illustrated in Table 3 which compares CH- and OH-acidities for similar structures. In water, the acidities of the CH-acids are, on the average, 20 pKa units lower than those of the respective OH-acids.

TABLE 3

Substituent effect on acidities of related OH- and CH-
acids; pKa=-logKa; ΔpKa's correspond to the differences
between pKa's of CH- and OH-acids of similar structure;
All pKa's (except for methane) are based on the equilibria



Acid	pKa	ΔpKa	Reference
H-OH	15.7	>25	2
H-CH ₂ H	>40*		
H-OCOCH ₃	4.7	ca.16	19
H-CH ₂ COCH ₃	ca.21		2
H-OCN	3.7	ca.20	20
H-CH ₂ CN	ca.24		2
H-ONO ₂	ca -7	ca.17	21
H-CH ₂ NO ₂	10.2		22

* See section III of this Chapter.

However, there do exist CH-acids which are strong even in water. Table 4 lists pKa values for some CH-acids measured in water; much more extensive data on the subject have been published by Ebel²³.

TABLE 4

CH-Acidities in water at 25°C

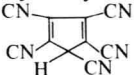
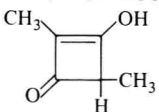
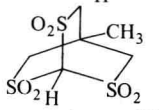
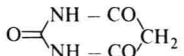
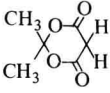
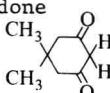

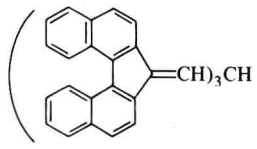

Compound	pKa	Reference
1. Pentacyanocyclopentadiene 	(-II)	24
2. Cyanoform $\text{HC}(\text{CN})_3$	(-5,13)	25
3. Nitroform $\text{HC}(\text{NO}_2)_3$	0.17	26
4. Acid dimer of methyl ketene 	2.8	27
5. 	3.30	28
	3.57	29.30
	3.60	31
6. Dinitromethane $\text{CH}_2(\text{NO}_2)_2$	3.47	32
7. Barbituric acid 	4.0	33
8. Trifluoroacetylacetone $\text{F}_3\text{C}-\text{CO}-\text{CH}_2\text{COCH}_3$	4.7	34
9. Meldrum acid 	4.83 (mixed acidity)	33
	2.49 (enol)	
10. 1,1-Dinitroethane $\text{CH}_3\text{C}(\text{NO}_2)_2\text{H}$	5.21	31
11. Nitroacetone $\text{O}_2\text{N}-\text{CH}_2-\text{CO}-\text{CH}_3$	5.1	34
12. Dimedone 	5.23 (pure enol)	
13. Cyclohexanedione-1,3 	5.26	36
14. Triacetyl methane $\text{HC}(\text{COCH}_3)_3$	5.81	37
15. Tris(7H-(dibenzo/c,g/fluorene)-ylidenemethyl) methane 		37

TABLE 4 (continued)

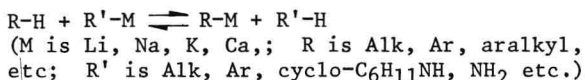
Compound	pKa	Reference
16. Ethyl fluoronitroacetate $\text{NO}_2\text{FHCCOOC}_2\text{H}_5$	6.28	39
17. Phenylnitromethane $\text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$	6.8 3.89 (aciform)	40
18. Dibenzoylmethane $\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$	8.95	41
19. Tetramethylmethylenedisulphonium $(\text{CH}_3)_2\text{S}^+-\text{CH}_2-\text{S}^+(\text{CH}_3)_2$	9.00	42
20. Acetylacetone $\text{CH}_3\text{COCH}_2\text{COCH}_3$	8.94 8.13 (enol)	35, 37
21. HCN	9.3	21
22. Nitromethane CH_3NO_2	10.21 10.24 10.1	22 43 44
23. Acetoacetic ester $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$	10.49 8.09 (enol)	35
24. Dicyanomethane $\text{CH}_2(\text{CN})_2$	11.19	34
25. Bis(phenylsulphonyl) methane $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_5$	11.21	45, 46
26. Malonic ester $\text{H}_2\text{C}(\text{COOC}_2\text{H}_5)_2$	13.30	34
27. Water H_2O	15.7	
28. Cyclopentanone 	16.7 11.8 (enol)	47
29. 4,4',4''-Trinitrotriphenylmethane $(4\text{-NO}_2\text{C}_6\text{H}_4)_3\text{CH}$	17.44 (in alcohol)	48

The CH-Acids listed at the start of Table 4 are comparable in their strength with inorganic acids such as perchloric and sulphuric acids. It is noteworthy that Table 4 contains few unsubstituted hydrocarbons. Except for the Kuhn hydrocarbon (No. 15 Table 4) all of the compounds have acidifying groups with electron-acceptor heteroatoms. Other compounds of the Kuhn type are shown in Table 21.

The equilibrium acidities of alkanes, alkenes, arenes, cycloalkanes and other weak CH-acids cannot be measured in hydroxyl-containing solvents. Molecules of H_2O in water have a rather high acidity (pKa 15.7). The acidities of hydrocarbons are usually measured in aprotic solvents. Methods for carrying out this measurement will be discussed in Section III.

III. METHODS OF MEASURING IONISATION EQUILIBRIA OF CH-ACIDS

Equilibrium acidity is a function of the equilibrium between an acid and the conjugated base. Equilibrium acidities of hydrocarbons are usually obtained from trans-metalation reactions in solvents of low polarity and low proton-donor activity, such as ether, benzene, liquid ammonia, cyclohexylamine, dimethylsulphoxide, etc.



In 1908 Shorygin showed that ethylsodium will metalate benzene, toluene, and diphenylmethane⁴⁹. This showed that methane is a weaker acid than are the other three. Following this, numerous qualitative data of the same kind were obtained; e.g., potassium amide in liquid ammonia did not metalate toluene but did metalate diphenylmethane⁵⁰, amylsodium reacted with benzene while phenylsodium, in turn, did so with toluene⁵¹. These data have been summarised in the acidity series⁵² pentane (or ethane) < benzene < toluene < NH₃ < diphenylmethane.

Much of this information was obtained in the late thirties⁵³⁻⁵⁸. However, it is only recently that a quantitative approach has been made by Conant and Wheland⁵⁹, and McEven⁶⁰ in their classical papers on this subject.

1. Trans-Metalation Equilibria

To estimate the relative acidities of hydrocarbons, Conant and Wheland⁵⁹ employed colorimetry. Conant and Wheland studied the equilibria of sodium or potassium salts of CH-acids in ether and McEven used benzene.



The salts RM and R'M absorb at different wavelengths, so the concentrations of these may be measured colorimetrically. The change in colour is, as a rule rapid, but in some cases (especially with sodium salts) many days are necessary for the equilibrium to be achieved. With the equilibrium (1) we have

$$\text{pKa}(\text{RH}) - \text{pKa}(\text{R}'\text{H}) = -\log \frac{[\text{RM}]}{[\text{RH}]} + \log \frac{[\text{R}'\text{M}]}{[\text{R}'\text{H}]} \quad (2)$$

At first McEven⁶⁰ believed that RM and R'M dissociated to the same extent whereas CH-acids did not dissociate at all. This led him to develop the following equation.

$$\text{pKa}(\text{RH}) - \text{pKa}(\text{R}'\text{H}) = -\log \frac{[\text{R}^-]}{[\text{RH}]} + \log \frac{[\text{R}'^-]}{[\text{R}'\text{H}]}$$

Later it was shown, however, that the sodium or caesium salts of fluorene in tetrahydrofuran at 25°C are intimate ion-pairs while the lithium salt is a solvent-separated ion-pair. Its visible spectrum coincides with, while the ultraviolet spectrum differs from, the spectra of the intimate pairs⁶². The electroconductivity data show that the fluorene salts dissociate to a small extent only. Thus, the change in colour observed by McEven⁶⁰ was due to ion-pairs rather than free ions, in other words, the Cram² equation (eq. 2) is valid.

Equation (2) says that the acids RH and R'H differ by two pKa units when the visual observation shows approximately 91% extent of metalation at the initial concentrations ratio of 1:1. If the same extent of metalation is achieved at a five-fold excess of R'H, the difference will be just 0.4 pKa units.

McEven⁶⁰ compared many pairs of CH-acids. He also collated the colorimetry data with the carboxylation data. The position of the equilibrium between