ADVANCES IN

Physical Organic Chemistry

VOLUME 35

Advances in Physical Organic Chemistry

Volume 35

Edited by

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ACADEMIC PRESS
A Harcourt Science and Technology Company

San Diego San Francisco New York
Boston London Sydney Tokyo

This book is printed on acid-free paper.

Academic Press
A Harcourt Science and Technology Company
Harcourt Place, 32 Jamestown Road, London NW1 7BY, UK
http://www.academicpress.com

Academic Press
A Harcourt Science and Technology Company
525 B Street, Suite 1900, San Diego, California 92101-4495, USA
http://www.academicpress.com

ISBN 0-12-033535-2

A catalogue record for this book is available from the British Library

This serial is covered by The *Science Citation Index*.

Typeset by Paston Prepress Ltd, Beccles, Suffolk

Printed and bound in Great Britain by
MPG Books Ltd, Cornwall, UK

00 01 02 03 04 05 MP 9 8 7 6 5 4 3 2 1

Advances in Physical Organic Chemistry

ADVISORY BOARD

Editor's preface

This volume is the first since Donald Bethell served as Editor of the series, and he set a very high standard both for the quality of the contributions presented and for the excellence of the editorial work. It is my hope as the new Editor to maintain this high level, and continue to provide the chemical community with authoritative and critical assessments of different aspects of the field of physical organic chemistry. The chapters in the previous volumes provide a lasting record that is widely cited and used, and will continue to serve for decades to come. Because this series has maintained such a high level of quality and utility there is little need for change, and one of the few innovations is the adoption of the numerical system of reference citation now used by almost all chemical journals.

The four chapters in this volume are intimately related to the study of carbocations and of free radicals, which are two classes of intermediates that were both recognized as discrete reactive intermediates just at the beginning of the twentieth century. The first chapter, on excess acidities, is a lucid exposition of the current understanding of a field that has been relevant to many of the great triumphs of physical organic chemistry throughout the century. The second chapter, on the behavior of carbocations in solution, demonstrates the exquisite detail with which these processes may now be understood. Two chapters concern electron transfer, and thus involve not only free radicals but charged species as well.

I wish to extend my thanks to the authors of the chapters in this volume for the uniformly high quality and timeliness of their contributions. The Advisory Board has been generous with their suggestions, and the success of this series is due in no small part to their efforts. Regretably the Board has suffered the loss of the services of Lennart Eberson, who died in February, 2000, and will be remembered as a distinguished chemist, a longtime contributor to this series, and a valuable member of the Board.

The new century is a time of great opportunity for physical organic chemistry, which in recent decades has expanded far beyond its traditional boundaries. This now encompasses fields ranging from the purely theoretical to the largely applied, and includes chemistry in the gas, liquid, and solid phases, and many aspects of biological, medicinal, and environmental chemistry. It is our intention to cover as many of these areas as possible.

It is also a time for reflection, for as I have discussed elsewhere (*Pure and Applied Chemistry* (1997), **69**: 211–213), the history of the field of physical organic chemistry belongs almost completely in the twentieth century. Thus the seminal recognition of reactive intermediates including carbocations, free radicals, and carbenes came very early in the century, along with the mechanistic and theoretical tools needed for understanding and interpreting the behavior of these species. Throughout the century the achievements of physical organic chemistry have been widely recognized, not least by the award of the Nobel Prize. In the past decade these prizes have honoured the theory of electron transfer reactions (R. Marcus, 1992), the direct observation of carbocations (G. A. Olah, 1994), molecular orbital calculations (J. Pople and W. Kohn, 1998), and the study of transition states (A. Zewail, 1999). All of these areas are central to the modern practice of physical organic chemistry, and the other prizes in this same period all show the influence of physical organic thinking. The twenty-first century offers even more opportunities, and *Advances in Physical Organic Chemistry* will aspire to bring the best of these to the chemical public.

As Editor I feel an obligation to continue the enviable record of this series, and to provide at reasonable cost a service to the users. Suggestions for prospective fields or authors are welcome.

T. T. Tidwell

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Contents

Excess Acidities

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1 Introduction

Large numbers of reactions of interest to chemists only take place in strongly acidic or strongly basic media. Many, if not most, of these reactions involve proton transfer processes, and for a complete description of the reaction the acidities or basicities of the proton transfer sites have to be determined or estimated. These quantities are also of interest in their own right, for the information available from the numbers via linear free energy relationships (LFERs), and for other reasons.

It is therefore necessary to have methods of dealing with kinetic and equilibrium data obtained in these media. Many chemists are convinced that

ADVANCES IN PHYSICAL ORGANIC CHEMISTRY
VOLUME 35 ISBN 0-12-033535-2

trying to use information obtained in strong acid or strong base media for the determination of the mechanisms of reactions is fraught with difficulty and complication. The most notorious example of this is R. P. Bell leaving out of the second edition of his book *The Proton in Chemistry*[1] the chapter on concentrated solutions of acids and bases that had been included in the first edition,[2] "partly because the interpretation of reaction velocities in these concentrated solutions has become more rather than less confused with the passage of time". It is my intention to present a simple, unified method of dealing with these systems, called the "excess acidity" method; to show that reasonably reliable thermodynamic acidity constants can be obtained by using it; and to show that the method leads to mechanistic information that is difficult if not impossible to obtain in any other way when used with kinetic data.

Space considerations permit only the consideration of strong aqueous acid media in this review, primarily H_2SO_4, $HClO_4$ and HCl. An equivalent technique (the "excess basicity" method) can be applied to strongly basic media; for instance, it has been applied to weak acidity determinations in aqueous dimethyl sulfoxide mixtures,[3–6] and used for kinetic studies in this system.[7] Sulfamide ionizations have been studied,[8] and ground and excited state acidities in other aqueous media have been determined.[9] The excess basicities of methanolic methoxide solutions have been examined,[10] and kinetics in these solutions have been looked at.[11,12] However, by and large strong bases have not been studied to nearly the same extent that strong acids have.

2 Determination of weak basicities

AQUEOUS SOLUTION

Since the days of Brønsted[13] the strengths of acids in aqueous solution have been defined in terms of the equilibrium constant K_a for the ionization of HA, equation (1):

$$\mathrm{HA} + \mathrm{H_2O} \overset{K_a}{\rightleftharpoons} \mathrm{H_3O^+} + \mathrm{A^-} \tag{1}$$

$$K_a = \frac{C_{\mathrm{H_3O^+}} C_{\mathrm{A^-}}}{C_{\mathrm{HA}}} \tag{2}$$

with the mathematical definition of K_a being that of equation (2) and C being molar concentration, which can be used in dilute solution. (According to Bell,[1] Lowry[14] and Lewis[15] were proposing somewhat similar ideas at the same time but did not give the actual definition according to equation (2).) Other states of protonation are possible in equation (1), for instance $H_2A^+ \rightarrow HA + H^+$, or $HA^- \rightarrow A^{2-} + H^+$, but for simplicity equation (2) will be used exclusively for $HA \rightarrow A^- + H^+$.

In equation (2), by convention (since it is in large excess when HA is in dilute solution) the concentration of water, C_{H_2O}, is *left out* of the definition. This leads to problems. For instance, when hydronium ion itself is the acid, for consistency equation (3) must be written:

$$H_3O^+ + H_2O \overset{K_a}{\rightleftharpoons} H_2O + H_3O^+ \tag{3}$$

$$K_a = \frac{C_{H_2O}C_{H_3O^+}}{C_{H_3O^+}} = C_{H_2O} = 55.34\,\text{M at } 25°\text{C} \tag{4}$$

and the K_a of water is defined according to equation (4), which leads to the pK_a of water being -1.743 rather than 0.000. (Similarly its pK_b is 15.743, not 14.000.)

In strong acids the convention is to write the protonation equilibrium of a weak base B as equation (5); the species H_3O^+ in equation (1) (or such higher proton solvates as may be present) is just written as "H^+" for simplicity, without indicating its structural environment:

$$B + H^+ \overset{K_{BH^+}}{\leftrightharpoons} BH^+ \tag{5}$$

The mathematical definition of K_{BH^+} is like that of K_a (now right-to left, see equation (5)); writing a for activities and f for molar activity coefficients, as is commonly done in strong acid work, equation (6) is obtained:

$$K_{BH^+} = \frac{a_B a_{H^+}}{a_{BH^+}} = \frac{C_B C_{H^+}}{C_{BH^+}} \cdot \frac{f_B f_{H^+}}{f_{BH^+}} \tag{6}$$

Note that the water activity is left out of the definition of K_{BH^+} in just the same way as it is for the definition of K_a in dilute aqueous solution. This is not necessarily a good idea in these non-ideal strong acid media, since the water activity can vary drastically as the medium changes from dilute to concentrated acid;[16–19] by no means does it remain constant, as the dilute solution definition implies, and so from this point of view it would be a good idea to include it. However, there are several practical problems involved if this is done. First, it would be necessary to alter either all listed pK_a values or all listed pK_{BH^+} values by 1.743 as given above, to allow comparison between values determined in aqueous buffers and those determined in strong acid. This seems an unnecessary complication. Secondly, the activities of water (and of the acid) have all been measured using the mole fraction activity scale,[16–19] which has the standard state (where $f = 1$) defined as being the pure solvent. Now this is different from the standard state used in equation (6), where $f = 1$ is defined as being infinite dilution in the reference medium, which is a hypothetical ideal solution 1 M in the acid being used, the same reference medium as that used for pH measurements.[20] Thus, before water activities can be included in the definition it is necessary to convert the listed mole fraction-based water activities to concentration-based ones, which is not a trivial operation. (The standard state for water now looks a bit strange, being an infinitely dilute solution of water in itself!) By and large it seems a lot easier to stay with the definition of equation (6). Nevertheless, there is one case where it is necessary to have these molarity-based water activities for equilibrium measurements, for the determination of $\mathrm{p}K_{\mathrm{R}^+}$ values, and they are also needed in kinetic studies, see below.

STRONG ACID MEDIA

$$\mathrm{p}K_{\mathrm{BH}^+} = \log I - \log C_{\mathrm{H}^+} - \log \frac{f_{\mathrm{B}} f_{\mathrm{H}^+}}{f_{\mathrm{BH}^+}} \tag{7}$$

Writing equation (6) in logarithmic form results in equation (7). Again by convention, the log ionization ratio, $\log I = \log(C_{\mathrm{BH}^+}/C_{\mathrm{B}})$, is defined, with the ionized form on top. Equations (6) and (7) are thermodynamically exact; the problem with them has always been what to do about the unknown activity coefficient ratio term. The first person to tackle this problem was Hammett,[21,22] who defined an acidity function, H_0, as in equation (8):

$$H_0 = \mathrm{p}K_{\mathrm{BH}^+} - \log I = -\log C_{\mathrm{H}^+} - \log \frac{f_{\mathrm{B}} f_{\mathrm{H}^+}}{f_{\mathrm{BH}^+}} \tag{8}$$

H_0 is defined so as to be similar to pH, and to reduce to it in dilute solution, i.e. to $\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} - \log I$. The idea is that versions of equation (8) can be written for weak base indicators that protonate to different extents in the same acid solutions (overlapping indicators; indicators because they indicate the solution acidity); subtracting two of these (say for indicators A and B) leads to equation (9), and if the activity coefficients for A and B, and for AH^+ and BH^+, approximately cancel, the value of $\mathrm{p}K_{\mathrm{BH}^+}$ can be calculated from the measured ionization ratios for A and B if $\mathrm{p}K_{\mathrm{AH}^+}$ is known:

$$\mathrm{p}K_{\mathrm{BH}^+} - \log \frac{C_{\mathrm{BH}^+}}{C_{\mathrm{B}}} - \mathrm{p}K_{\mathrm{AH}^+} + \log \frac{C_{\mathrm{AH}^+}}{C_{\mathrm{A}}} = \log \frac{f_{\mathrm{A}} f_{\mathrm{BH}^+}}{f_{\mathrm{AH}^+} f_{\mathrm{B}}} = 0 \tag{9}$$

A is an *anchor compound*, one whose ionization ratios are measurable in dilute aqueous acid; $\mathrm{p}K_{\mathrm{BH}^+} = 1.00$ for *p*-nitroaniline is used for H_0.[22,23] Equation (9) is known as the *cancellation assumption*; using it on a series of overlapping weak base indicators of similar type (primary aromatic amines in the case of H_0) leads to H_0 values covering a wide acidity range according to equation (8), once all the $\mathrm{p}K_{\mathrm{BH}^+}$ values are known.

It was soon realized that there are problems with this approach.[24,25] Log ionization ratios for weak bases that are not primary aromatic amines, while linear in H_0, do not give the unit slope required by equation (8). This soon led to many other acidity functions, defined for other types of weak base, H_{A} for amides,[24] H_0''' for tertiary aromatic amines,[25] C_0 or H_{R} for carbocations,[26,27] and so on. In a recent review of acidity functions,[28] 28 different ones were listed for aqueous sulfuric acid mixtures alone! So H_0 is not a universal function, although it can still be used to obtain values for the pK_{BH^+} of other types of compound. There are two ways of doing this in common use; the first, sometimes referred to as the Yates–McClelland method,[29] is simply to accept a slope m other than unity and use equation (10); the pK_{BH^+} is then (mH_0) when $\log I$ is zero (half-protonation):

$$\log I = m(-H_0) + pK_{BH^+} \tag{10}$$

The second way, called the Bunnett–Olsen method,[30] makes the less drastic assumption that log activity coefficient ratios such as those in equation (7) are linear functions of one another, rather than cancelling out. From the definition of H_0 in equation (8) we can write equation (11), where Am refers to the primary aromatic amines used in the determination of H_0, and then any specific activity coefficient ratio, say for the weak base B, is assumed to be linear in this according to equation (12):

$$H_0 + \log C_{H^+} = -\log \frac{f_{Am} f_{H^+}}{f_{AmH^+}} \tag{11}$$

$$\log \frac{f_B f_{H^+}}{f_{BH^+}} = (1 - \phi_e) \log \frac{f_{Am} f_{H^+}}{f_{AmH^+}} \tag{12}$$

Equation (12) is a linear free-energy relationship, since activity coefficients f can be represented as ΔG° values. The reason for defining the slope parameter as in equation (12) (subscript e for equilibrium) is that a little rearranging of equations (11) and (12) leads to the easy-to-use Bunnett–Olsen equation for equilibria, equation (13):[30]

$$\log I + H_0 = pK_{BH^+} + \phi_e(H_0 + \log C_{H^+}) \tag{13}$$

This linear plot works very well, giving pK_{BH^+} values as intercepts (and slopes ϕ_e); thus only one acidity function (H_0) is needed for the purpose of estimating weak basicities. In the Bunnett–Olsen method C_{H^+} is simply the acid molarity. The terms m from the Yates–McClelland method and $(1 - \phi_e)$ from the Bunnett–Olsen method are, for all practical purposes, equivalent: $m = {\sim}1$, $\phi_e = {\sim}0$ for primary nitroanilines; $m = {\sim}0.6$, $\phi_e = {\sim}0.4$ for amides; and so on.

3 The excess acidity method

A philosophical problem remains, however. The Bunnett–Olsen method, which assumes the linearity of activity coefficient ratios in one another, still uses H_0, and H_0 values are derived using the cancellation assumption! The cancellation assumption is eliminated altogether in the *excess acidity method* (also called the Marziano–Cimino–Passerini and Cox–Yates methods, which is unfortunate since both are the same – the term "excess acidity method" is preferred).

For an anchor compound B* (say *p*-nitroaniline), whose ionization ratios are measurable in dilute acid, we can write the thermodynamically exact equation (14):

$$\log I_{\mathrm{B}^*} - \log C_{\mathrm{H}^+} = \log \frac{f_{\mathrm{B}^*} f_{\mathrm{H}^+}}{f_{\mathrm{B}^*\mathrm{H}^+}} + \mathrm{p}K_{\mathrm{B}^*\mathrm{H}^+} \tag{14}$$

For an overlapping indicator B′ we can write equation (15):

$$\begin{aligned} \log I_{\mathrm{B}'} - \log C_{\mathrm{H}^+} &= \log \frac{f_{\mathrm{B}'} f_{\mathrm{H}^+}}{f_{\mathrm{B}'\mathrm{H}^+}} + \mathrm{p}K_{\mathrm{B}'\mathrm{H}^+} \\ &= n_1 \log \frac{f_{\mathrm{B}^*} f_{\mathrm{H}^+}}{f_{\mathrm{B}^*\mathrm{H}^+}} + \mathrm{p}K_{\mathrm{B}'\mathrm{H}^+} \\ &= n_1 (\log I_{\mathrm{B}^*} - \log C_{\mathrm{H}^+} - \mathrm{p}K_{\mathrm{B}^*\mathrm{H}^+}) + \mathrm{p}K_{\mathrm{B}'\mathrm{H}^+} \end{aligned} \tag{15}$$

giving n_1 and $\mathrm{p}K_{\mathrm{B}'\mathrm{H}^+}$ from the resulting linear plot, and enabling further values of the activity coefficient ratio for B* to be calculated. This process can be continued into stronger and stronger acid media. This technique was originally formulated by Marziano, Cimino and Passerini,[31] who abbreviated the activity coefficient ratio term for B* as M_C (equation 16), and the slopes as *n*, later $n_{i,j}$.[32] These authors provided several scales for aqueous H_2SO_4 and $HClO_4$ media.[31]

$$\log \frac{f_{\mathrm{B}^*} f_{\mathrm{H}^+}}{f_{\mathrm{B}^*\mathrm{H}^+}} = M_\mathrm{C} \quad \text{or} \quad X \tag{16}$$

Subsequently the calculation of M_C (now called $M_\mathrm{C}f(x)$) was improved by mathematical treatment.[33] The assumption upon which the method is based, linearity according to equation (15), has been thoroughly tested for aqueous $HClO_4$[32] and H_2SO_4[34] media. Cox and Yates[20] computerized the calculation of these functions, preferring the simpler terminology *X* for "excess acidity", since the activity coefficient ratio represents the difference between the actual solution acidity and the stoichiometric acid concentration, and m^* for the slopes, as in equation (17). The term excess acidity was first used by Perrin,[35] although he defined it in Bunnett–Olsen terms as being $(-H_0 - \log[\mathrm{H}^+])$, see equation (11), which is somewhat different from the current equation (16) definition.

EXCESS ACIDITY SCALES

$$\log I - \log C_{\mathrm{H}^+} = m^* X + \mathrm{p}K_{\mathrm{BH}^+} \tag{17}$$

Equation (17) is the heart of the excess acidity method for the determination of unknown $\mathrm{p}K_{\mathrm{BH}^+}$ values in strongly acidic media. Without going into detail (which is tedious) polynomial coefficients have been calculated that enable the calculation of *X* for 0–99.5 wt% H_2SO_4 and 0–80 wt% $HClO_4$. These are used with equation (18) and are given in Table 1. The form of equation (18) was

Table 1 Polynomial coefficients giving X as a function of wt% acid at 25°C for aqueous sulfuric and perchloric acid mixtures.[a]

Polynomial coefficient	Gives X for aq. H_2SO_4	Gives X for aq. $HClO_4$
a_1	−1.2192412	−0.74507718
a_2	1.7421259	1.0091461
a_3	−0.62972385	−0.30591601
a_4	0.11637637	0.049738522
a_5	−0.010456662	−0.0040517065
a_6	0.00036118026	0.00012855227

[a] From ref. 20. Use with equation (18).

chosen in order to have $X = 0$ in pure water, and to provide polynomial coefficients near to unity:

$$X = a_1(z-1) + a_2(z^2-1) + a_3(z^3-1) + \cdots$$
$$z = \text{antilog}(\text{wt\%}/100) \text{ for } H_2SO_4; \quad z = \text{antilog}(\text{wt\%}/80) \text{ for } HClO_4 \tag{18}$$

Subsequently this computer method was investigated in more detail,[36] and it was found that it was not necessary to be as elaborate as equation (18). The polynomial coefficients given in Table 2 for HCl and $HClO_4$ are used with the much simpler equation (19):

$$X = a_1(\text{wt\%}) + a_2(\text{wt\%})^2 + a_3(\text{wt\%})^3 \tag{19}$$

The X_0 scale for $HClO_4$ that can be obtained from Table 2 is derived using H_0 indicators only (primary aromatic amines), rather than the broad mix of indicators of different type used in deriving X. Values of X calculated from these polynomial coefficients are given for H_2SO_4 in Tables 3 and 4, for $HClO_4$ in Tables 5 and 6 (with X_0), and for HCl in Tables 7 and 8, as a function of wt% acid (odd-numbered tables) and of the acid molarity (even-numbered tables).

Other information is provided in Tables 3–8. This includes values of $\log C_{H^+}$ for use with equation 17; for $HClO_4$ and HCl these are simply the log acid molarity, assuming the acid to be fully dissociated. The maximum acid strength is 80 wt% for $HClO_4$, at which point the acid mixtures become solid at 25°C, and 40% for HCl, at which point the aqueous solution is saturated with the

Table 2 Polynomial coefficients giving X as a function of wt% acid at 25°C for aqueous hydrochloric acid mixtures, and X_0 at 25°C for aqueous perchloric acid mixtures.[a]

Polynomial coefficient	Gives X for aq. HCl	Gives X_0 for aq. $HClO_4$
a_1	0.0527767	0.0335096
a_2	0.00190497	−0.000745044
a_3	−0.0000197423	0.0000222391

[a] From ref. 36. Use with equation (19).