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Intramolecular Hydrogen Bonding in Monoanions of o-Phthalic Acid and the Homologous Oxalic Acid Series in Acetonitrile

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Abstract: First and second dissociation constants, K_1 and K_2, and homoconjugation constants, K_{homo}, of the homologous series of oxalic to azelaic acids, fumaric acid, and o-phthalic acid (H_2A), have been determined in acetonitrile. Also presented are the dissociation constant $K(HE)$ and homoconjugation constant $K(HE_2^-)$ of the corresponding mono methyl or ethyl esters (HE). Using these data and eq 1, the following values of $K' = [\overline{HA^-}]/[HA^-]$, $\overline{HA^-}$ denoting the intramolecular hydrogen-bonded species, have been found: malonic 2.5×10^4, succinic 5×10^3, glutaric 6×10^2, adipic 4×10^1, azelaic 1.5×10^1, o-phthalic 3×10^5. The intramolecular hydrogen bond in $\overline{HA^-}$ is quite stable, but the strength of this bond decreases with increasing distance between the carboxyl groups. No indication of $\overline{HA^-}$ species has been found in the monofumarate ion. In all of the above acids the homoconjugate $(\overline{HA}-H_2A)^-$ is present in excess over $(HA-H_2A)^-$, the ratio $[\overline{H_3A_2^-}]/[H_3A_2^-]$ decreasing as K' decreases. Evidence has been presented that the monoesters and the diacids are not intramolecularly hydrogen bonded in acetonitrile.

Hunter[1] attributed abnormally large ratios of the first to the second dissociation constants K_1/K_2 of many dicarboxylic acids, H_2A, to intramolecular hydrogen bonding in the monoanion, $\overline{HA^-}$. In accordance with this interpretation, Brown[2] stated that strain as a result of steric crowding of the carboxyl groups is relieved to some extent by formation of the intramolecularly hydrogen-bonded monoanion. Examples cited are alkyl-substituted succinic, malonic, and maleic acids. Very large values of K_1/K_2 have been obtained by Eberson[3] for rac-α,α'-dialkylsuccinic acids in 50% water-ethanol mixtures. A quantitative treatment of the effect of intramolecular hydrogen bonding in HA^- was given by Westheimer and Benfy.[4] They considered that in the familiar expression of K_1 the anion concentration is equal to $[HA^-] + [\overline{HA^-}]$, $[\overline{HA^-}]$ denoting the intramolecular hydrogen bonded form of the monoanion. They made the reasonable assumptions that the inductive effect of the carboxyl groups in the diacid H_2A and the carbalkoxyl group in the monoester HE are the same and that intramolecular hydrogen bonding in H_2A and HE is absent. Thus, for statistical reasons, K_1 should be equal to $2K(HE)$ in the absence of intramolecular hydrogen bonding in the monoanion. When there is intramolecular hydrogen bonding, relation 1 is easily derived. In eq 1, K' is the equilibrium

$$K' = [\overline{HA^-}]/[HA^-] = K_1/2K(HE) - 1 \qquad (1)$$

constant of the reaction $HA^- \rightleftarrows \overline{HA^-}$. From known values of K_1 and $K(HE)$ they concluded that in aqueous medium intramolecular hydrogen bonding between the carboxyl and carboxylate groups in HA^- is absent in the homologous series beginning with oxalic acid and in o-phthalic acid, since $K_1 \sim 2K(HE)$. In aqueous solution there is strong hydrogen bonding of the carboxylate and, to a much smaller extent,

of the carboxyl group to the solvent, thus stabilizing HA^- at the expense of $\overline{HA^-}$. Water is a much stronger base[5] and acid and also a stronger hydrogen bond acceptor and much stronger hydrogen bond donor than acetonitrile (AN). Hydrogen bonding of a carboxyl group with a dipolar protophobic solvent like AN is considerably weaker than that in water,[6] while the hydrogen bonding of the carboxylate ion with AN appears to be negligible.[6] Thus, it is to be expected that sizable values of K' in eq 1 may found in AN for o-phthalic acid and the homologous series of oxalic acid and that K' decreases with the number of -CH₂- groups.

In the present paper are presented values of pK_1, pK_2, and $pK(HE)$ at 25° of oxalic, malonic, succinic, glutaric, adipic, azelaic, o-phthalic, and fumaric acids and their monomethyl or monoethyl esters in acetonitrile. Values of paH were determined potentiometrically with the glass electrode in mixtures of the diacids and their monotetraethylammonium salts and in mixtures of the mono- and ditetraethylammonium salts. To avoid decomposition of the tetraalkylammonium salts of the monoester acids, mixtures of HE and freshly prepared ~ 1 M tetramethylammonium hydroxide solution in methanol were used. Correction was made for the effect on paH by the methanol thus introduced.

Homoconjugation constants have been calculated from paH values in mixtures of the diacid and its monoanion.[7] Considering that the monoanion is partly present as $\overline{HA^-}$ and partly as HA^-, and assuming that only the latter can intermolecularly hydrogen bond with H_2A to form the homoconjugate $H_3A_2^-$, expression 2 would be

$$K_{homo} = [H_3A_2^-]/([H_2A]([HA^-] + [\overline{HA^-}])) \qquad (2)$$

where K_{homo} is the observed homoconjugation constant. In the absence of intramolecular hydrogen bonding in HA

$$K(\mathrm{H_3A_2^-}) = [\mathrm{H_3A_2^-}]/[\mathrm{H_2A}][\mathrm{HA^-}] \qquad (3)$$

Substituting eq 1 and 3 into eq 2, eq 4 results. On statistical

$$K_{\mathrm{homo}} = \frac{K(\mathrm{H_3A_2^-})}{1 + K'} = \frac{2K(\mathrm{H_3A_2^-})K(\mathrm{HE})}{K_1} \qquad (4)$$

grounds and assuming[4] the inductive effect of the carboxyl and carbalkoxyl groups to be equal, $K(\mathrm{H_3A_2^-}) = 2K(\mathrm{HE_2^-})$. Equation 4 becomes

$$K_{\mathrm{homo}} = 2K(\mathrm{HE_2^-})/(1 + K') \qquad (5)$$

To test eq 5, homoconjugation constants of diprotic acids and their methyl esters have been estimated from paH values of mixtures of the acids and their monotetraethylammonium salts.

Heteroconjugation constants with chloride of glutaric, butyric, and monomethyl glutarate have been estimated in order to find indication of intramolecular hydrogen bonding in glutaric acid and/or its monoester.

Osmometric measurements have been carried out with solutions of tetraethylammonium bisuccinate to test whether dimerization occurs and to check the homoconjugation constant by an independent method in mixtures of this salt with succinic acid.

Experimental Section

Chemicals. Acetonitrile was purified and dispensed as described previously.[8] Its water content by Karl Fischer titration was 0.004 M. Dimethyl sufoxide[9] and methanol[10] were products used previously.

Acids. o-Phthalic and malonic acids were Matheson Coleman and Bell products. They were recrystallized from acetonitrile; the other acids were used without recrystallization. Oxalic acid dihydrate was a Baker Co. product; it was converted to the anhydrous form by drying at room temperature for a week over sulfuric acid, then for 2 days over phosphorus pentoxide. Succinic acid was a Merck Co. product, while glutaric, adipic, azelaic, and fumaric acids were Eastman Kodak White Label products. After drying these acids for 2 hr at 60°, assay by alkalimetric titration in water yielded 100.0 ± 0.5%. Thus, no anhydride formation occurs under these conditions.

Esters. Monomethyl succinate, glutarate, and adipate were Aldrich Co. products used without further purification. Monomethyl fumarate was from Pfaltz & Bauer, while monomethyl phthalate was a K & K Co. product. They were recrystallized from AN–methanol mixtures. Monoethyl malonate was prepared from Baker Co. potassium salt by reaction with aqueous hydrochloric acid at 5° as described by Strube.[11] Alkalimetric assay in methanol–water mixtures (by weight) of the monoesters (by weight) were as follows: malonate 98.9%, succinate 103.0%, glutarate 99.9%, adipate 100.0%, fumarate 100.7%, and o-phthalate 100.0%.

Salts. Tetraethylammonium binoxalate, oxalate, bisuccinate, and succinate were prepared by Smagowski in this laboratory.[12] Mono- and ditetraethylammonium salts of malonic, glutaric, adipic, and o-phthalic acids and the biazelate salt were prepared by neutralization of 20–50 ml of 2 M solutions of the diacids in methanol with 1 M tetraethylammonium hydroxide in methanol. The hydroxide solution was freshly prepared from Mallinckrodt Co. silver oxide and Eastman White Label tetraethylammonium bromide. Solutions of the normal salts were about 1–2% underneutralized to avoid decomposition of the tetraethylammonium ion in strongly alkaline solution. After evaporation of the solvent, the residues were taken to dryness under a heat lamp. The acid and normal salts of malonic, glutaric, and phthalic acids were recrystallized from ethanol–ethyl acetate mixtures. The acid and normal salts of fumaric and azelaic acid melted well below room temperature and could not easily be recrystallized.

All acid and normal tetraethylammonium salts were assayed by titration in AN with 0.5 M perchloric acid (in acetic acid) to the α-naphtholbenzein end point[13] and the acid salts by titration in water with sodium hydroxide to the phenolphthalein end point. The amount of acid salt in the normal salt was estimated by titration in water with sodium hydroxide. The sum of $[\mathrm{HA^-}] + 2[\mathrm{A^{2-}}]$
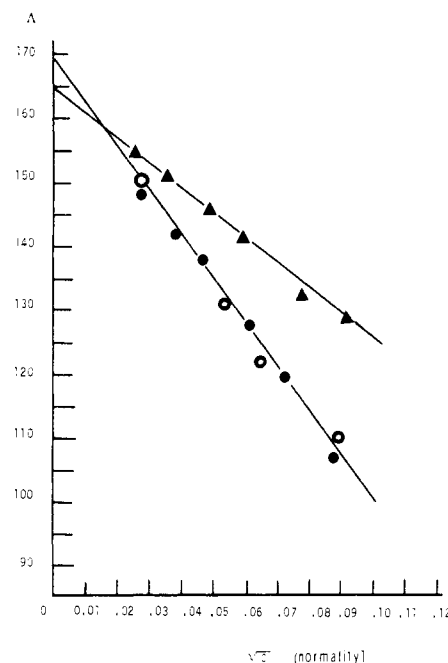

Figure 1. Plots of Λ vs. $\sqrt{c}$ of salts in acetonitrile: (▲) tetraethylammonium bimalonate; (●) malonate; and (○) succinate.

was titrated with standard perchloric acid and $2[\mathrm{H_2A}] + [\mathrm{HA^-}]$ with alkali. With many of the salts the sum of the percentages of $\mathrm{HA^-}$ and $\mathrm{A^{2-}}$ thus found was less than 100.0%, the difference between 100.0% and the sum denoted as n. No evidence of free $\mathrm{H_2A}$ was found in any of the acid salts. The water content of the salts was estimated by titration in methanol with Karl Fischer reagent.

Results of the assays of the salts expressed as percentages by weight are as follows (salt anion indicated in italics): HOx^- ($\mathrm{HOx^-}$ 96.6, $\mathrm{Ox^{2-}}$ 1.2, n 2.2); Ox^{2-} ($\mathrm{HOx^-}$ 0.1$_3$, $\mathrm{Ox^{2-}}$ 88.0, n 11.8, $\mathrm{H_2O}$ 10.0); $HMal^-$ ($\mathrm{HMal^-}$ 97.8, $\mathrm{Mal^{2-}}$ 0.5, n 1.7, $\mathrm{H_2O}$ 0.2); Mal^{2-} ($\mathrm{HMal^-}$ 4.4, $\mathrm{Mal^{2-}}$ 89.3, n 6.3, $\mathrm{H_2O}$ 7.7); $HSuc^-$ ($\mathrm{HSuc^-}$ 95.3, $\mathrm{Suc^{2-}}$ 3.1, n 1.6, $\mathrm{H_2O} \sim 0.1$); Suc^{2-} ($\mathrm{HSuc^-}$ 0.01, $\mathrm{Suc^{2-}}$ 94.4, n 5.6, $\mathrm{H_2O}$ 5.1$_5$); $HGlu^-$ ($\mathrm{HGlu^-}$ 98.6, $\mathrm{Glu^{2-}}$ 1.4, n 0.0); Glu^{2-} ($\mathrm{HGlu^-}$ 1.7, $\mathrm{Glu^{2-}}$ 89.8, n 8.5, $\mathrm{H_2O}$ 4.7); HAd^- ($\mathrm{HAd^-}$ 90.2, $\mathrm{Ad^{2-}}$ 1.2, n 8.6, $\mathrm{H_2O} \sim 0.3$); Ad^{2-} ($\mathrm{HAd^-}$ 3.0, $\mathrm{Ad^{2-}}$ 84.2, n 12.8, $\mathrm{H_2O}$ 1.8); HAz^- ($\mathrm{HAz^-}$ 92.8, $\mathrm{Az^{2-}}$ 7.2, $n \sim 0$); $HPth^-$ ($\mathrm{HPth^-}$ 100.0, $\mathrm{Pth^{2-}}$ 0.1, $n \sim 0$); Pth^{2-} ($\mathrm{HPth^-}$ 0.9, $\mathrm{Pth^{2-}}$ 88.5, n 10.6, $\mathrm{H_2O}$ 11.6). The following abbreviations were used: Ox = oxalate, Mal = malonate, Suc = succinate, Glu = glutarate, Ad = adipate, and Pth = phthalate. Potassium chloride was Mallinckrodt Analytical Reagent Grade, dried at 110°.

Techniques. The potentiometric assembly, glass and reference electrodes,[7] conductivity bridge and cell,[8] and osmometer[14] were described previously. All experiments were performed at 25°.

Results

Dissociation of Salts. Ionic Mobilities. The following ionic mobilities at infinite dilution have been reported previously: $\mathrm{Et_4N^+}$, 85;[15] $\mathrm{K^+}$, 85;[16] $\mathrm{Cl^-}$, 89;[17] $\mathrm{HA \cdot Cl^-}$, 45.[18] Conductance data of tetraethylammonium bimalonate, malonate, and succinate are presented as plots of Λ vs. $\sqrt{c}$ (c = normality) in Figure 1. The following values of $\lambda_0(\mathrm{HA^-})$ and $\lambda_0(\mathrm{A^{2-}})$ were found: bimalonate 79, malonate and succinate 85. For complete dissociation Onsager slopes of 351, 683, and 683 for bimalonate, succinate, and malonate, respectively, are expected, while the observed slopes were 380, 700, and 700, indicating essentially complete dissociation in the concentration range studied. From the fact that the osmometric molarity of tetraethylammonium bisuccinate is practically twice the analytical molarity to at least 0.02 M (Table II), one concludes that this electrolyte is completely dissociated in AN in the concentration range used. It is reasonable to assume that the other tetraethylammonium salts are also completely dissociated.
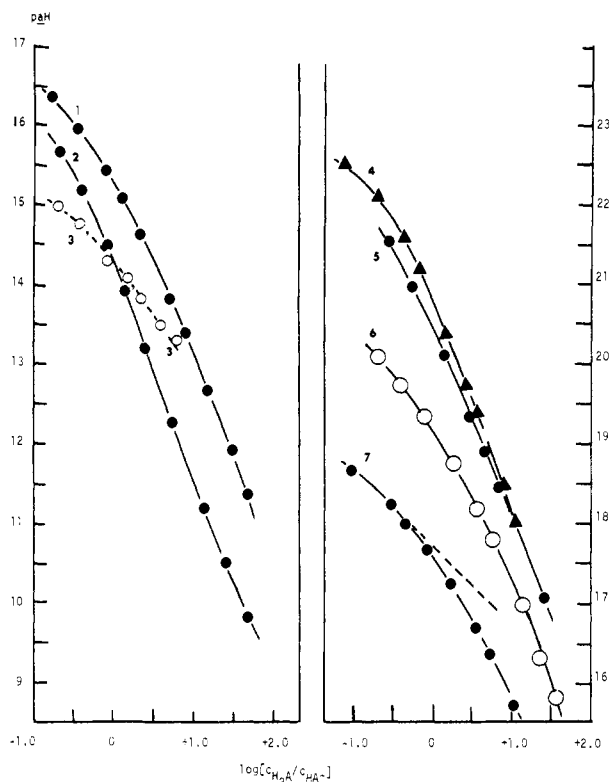
Figure 2. Plots of paH vs. log[$c_{H_2A}/c_{HA^-}f$] in mixtures of diacids with their tetraethylammonium acid salts: 1, malonic acid, c_{HA^-} = 0.0047 M; 2, oxalic acid, c_{HA^-} = 0.0049 M; 3, o-phthalic acid, c_{HA^-} = 0.0029 M; 4, azelaic acid, c_{HA^-} = 0.0047 M; 5, adipic acid, c_{HA^-} = 0.0038 M; 6, glutaric acid, c_{HA^-} = 0.0036 M; and 7, succinic acid, c_{HA^-} = 0.0057 M. Dashed line has slope of -1.0.

Values of pK_1, pK_2, pK(HE), and Homoconjugation Constants from Potentiometric Data.

Plots of paH vs. log $c_{H_2A}/c_{HA^-}f$ for oxalic, malonic, succinic, glutaric, adipic, azelaic, and o-phthalic acids constructed from data in mixtures of the diacids and their tetraethylammonium salts are presented in Figure 2. In Figure 3 are entered plots of paH (corrected for effect of water, $vide$ $infra$) vs. log $c_{HA^-}/c_{A^{2-}}f^3$ derived from data in mixtures of tetraethylammonium acid and normal salts of the above acids except azelaic. The partially extended Debye-Hückel expression was used to calculate activity coefficients of the anions; for univalent ions log f = 1.53$\sqrt{\mu}/(1 + 2.9\sqrt{\mu})$. A value of a^0 = 6 Å was used for all ions.

Since the normal salts contained appreciable amounts of water, the effect of small amounts of water on paH of the acid salt-normal salt mixtures, amounting to 0.1-0.3 paH unit, was taken into account. In the calculation of this effect the hydration constants of the acid salts were assumed to be the same as those of bisuccinate, $i.e.$, K^f(H$_2$O·$\overline{HSuc^-}$) = 5.0, K^f(3H$_2$O·$\overline{HSuc^-}$) = 2.8 (unpublished work), and those of the normal salts the same as for succinate, K^f(H$_2$O·Suc^{2-}) = 5 × 10^1, K^f(2H$_2$O·Suc^{2-}) = 1.7 × 10^4, K^f(4H$_2$O·Suc^{2-}) = 3.2 × 10^5 (unpublished work). Since homoconjugation does not occur in the monoanion-dianion systems, the following relation[19] was used to correct paH values for the effect of water: paH = paH$_0$ + log V/v, where V = 1 + K^f(H$_2$O·$\overline{HA^-}$)[H$_2$O] + ... and v = 1 + K^f(H$_2$O·A^{2-})[H$_2$O] + ... The effect of water in the system on paH of the diacid-monoanion mixtures is negligible (<0.1 unit), as the water content never exceeded 0.007 M and the hydration of HA$^-$ is much smaller than that of A^{2-}.

As the tetraalkylammonium salts of the monoesters and also tetraethylammonium bi- and normal fumarates and
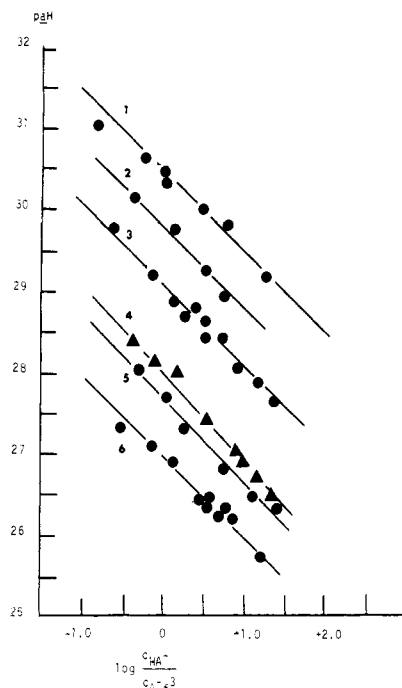
Figure 3. Plots of paH vs. log[$c_{HA^-}/c_{A^{2-}}f^3$] in mixtures of tetraethylammonium acid salts and normal salts: 1, malonate, $c_{A^{2-}}$ = 0.0029 M; 2, o-phthalate, $c_{A^{2-}}$ = 0.0025 M; 3, succinate, $c_{A^{2-}}$ = 0.0032 M; 4, glutarate, $c_{A^{2-}}$ = 0.0030 M; 5, oxalate, $c_{A^{2-}}$ = 0.0029 M; and 6, adipate, $c_{A^{2-}}$ = 0.0027 m. Slopes = -1.00 for malonate, phthalate, succinate, and adipate, -1.03 for oxalate, and -1.05 for glutarate.

azelates could not be readily prepared in a sufficiently pure form, paH values were estimated in various mixtures of the monoesters, azelaic or fumaric acids in AN with freshly prepared 1.1 M tetramethylammonium hydroxide in methanol. To find the effect of methanol thus introduced into equimolar mixtures of H$_2$A and HA$^-$ and of HA$^-$ and A^{2-} for fumaric and azelaic acids, increments of methanol were added and plots of paH vs. c_{MeOH} constructed, as presented in Figure 4. These plots were extrapolated to zero methanol concentration and from the resulting paH$_0$ values pK_1 and pK_2 were estimated. For H$_2$A-HA$^-$ mixtures the extrapolations amounted to only ~0.1 paH unit, while a larger extrapolation of 0.5-0.6 unit was required for the HA$^-$-A^{2-} mixtures, which results in an uncertainty of ±0.3 unit in pK_2 of azelaic and fumaric acids.

Plots of paH (uncorrected for effect of methanol) vs. log c_a/c_s are presented in Figure 5 for mixtures of monoethyl malonate, monomethyl succinate, glutarate, adipate, fumarate, and o-phthalate with tetramethylammonium hydroxide. The methanol concentration thus introduced varied from 0.02 to 0.12 M. Values of pK_{HE} were determined at the midpoint using the relation pK_a = paH$_{1/2}$ + log $V_{1/2}$ - log $f_{1/2}$, where V is defined as above, substituting methanol for water, and the subscript ½ denotes the midpoint. Values of K^f(MeOH·MeSuc$^-$) ~ 1, K^f(2MeOH·MeSuc$^-$) ÷ 4.6 × 10^1 and K^f(MeOH·MeHSuc) = 0 were derived[19] from the plots in Figure 4 (curves 3 and 5). Homoconjugation constants of the monoesters were evaluated from the data in Figure 5, using the following relation

$$K(HA_2^-) =$$
$$[c_s V_{1/2}r^2 - V V_{1/2}r(c_a + c_s) + V^2 c_a]/rV_{1/2}(c_a - c_s)^2$$

where r = $a_{H^+}/a_{H_{1/2}^+}$. Overall homoconjugation constants (K_{homo} = $K(\Sigma H_3 A_2^-)$) were calculated from the data in Figure 2, taking V = $V_{1/2}$ = 1. No evidence of homoconju-

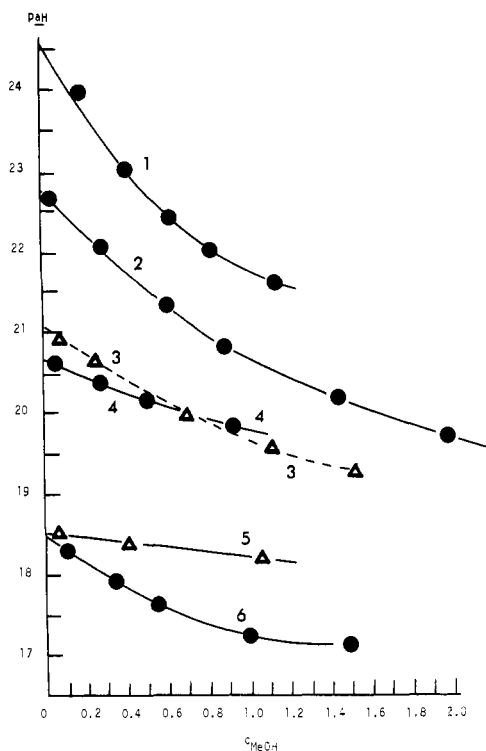Figure 4. Effect of methanol on paH of various acid–salt mixtures: 1, 0.0028 M Me$_4$NHAz, 0.0028 M (Me$_4$N)$_2$Az; 2, 0.0028 M Et$_4$NH-Fum, 0.0028 M (Et$_4$N)$_2$Fum; 3, 0.00400 M MeHSuc (monomethyl ester), 0.00334 M Me$_4$NMeSuc; 4, 0.0028 M H$_2$Az, 0.0028 M Me$_4$N-HAz; 5, 0.0203 M MeHSuc, 0.00279 M Me$_4$NMeSuc; and 6, 0.0024 M H$_2$Fum, 0.0024 M Et$_4$NHFum.

gation between HA$^-$ and A^{2-} is found from the plots in Figure 3 for any of the systems studied.

A summary of values of pK_1, pK_2, pK(HE), and homoconjugation constants of diacids and of monoesters is in Table I.

Osmometry. Osmometric molarities in mixtures of succinic acid and tetraethylammonium bisuccinate are compared in Table II with those calculated from $K_{homo} = 2.1 \times 10^2$. The bisuccinate salt has been regarded as being completely dissociated, and in addition, the bisuccinate ion and succinic acid are regarded as being monomeric. Hence $c_{Et_4NHSuc} = \Sigma[HA^-] + \Sigma[H_3A_2^-]$ and $c_{H_2Suc} = [H_2A] + \Sigma[H_3A_2^-]$. Satisfactory agreement is obtained between the observed and calculated osmometric molarities; when homoconjugation is assumed to be absent, the calculated osmometric molarities are considerably higher. For example, when $c_{H_2Suc} = 0.0184$, $c_{HSuc^-} = 0.0392$, the osmometric molarity (m) would be 0.0968 without homoconjugation, but when homoconjugation is considered $m = 0.0815$ as compared to the experimental value of 0.077.

Heteroconjugation of Acids with Chloride. In Figure 6 the effect of glutaric and butyric acids and monomethyl glutarate on the ionic solubility of potassium chloride in AN as determined conductometrically is presented as plots of $f^2[K^+]^2/K^{sp}(KCl)$ vs. c_{HA} as was done previously with other systems.[20] A value of $K^{sp}(KCl) = 1.1 \times 10^{-8}$ [20] was used. Viscosities of the solutions were assumed to be the same as those of the same concentrations of ethyl acetate.[5] The following values of the 1:1 heteroconjugation constants with chloride were found: glutaric acid, 2.8 $\times$ 10^2; monomethyl glutarate, 1.4$_5$ $\times$ 10^2; and butyric acid, 1.4 $\times$ 10^2. Values of the stepwise formation constants of the 2:1 conjugates from the 1:1 conjugates are 3.$_6$, 1.$_8$, and 1.$_6$, respectively.
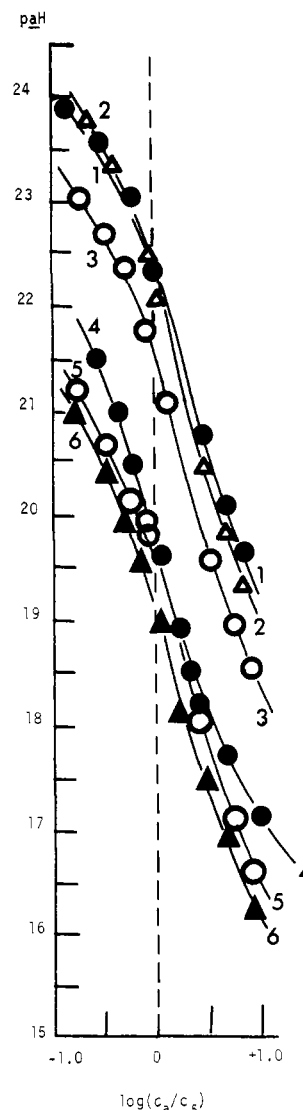

Figure 5. Plots of paH vs. log(c_a/c_s) in mixtures of monesters of diprotic acids and tetramethylammonium hydroxide: 1, monomethyl adipate, $c_s = 2.5 \times 10^{-3}$ to 5.1×10^{-3} M; 2, monomethyl glutarate, $c_s = 2.7 \times 10^{-3}$ to 5.6×10^{-3}; 3, monomethyl succinate, $c_s = 2.8 \times 10^{-3}$ to 6.1×10^{-3}; 4, monoethyl malonate, ($c_a + c_s$) = 6.73×10^{-3} M; 5, monomethyl phthalate, $c_s = 2.1 \times 10^{-3}$ to 4.2×10^{-3} M; and 6, monomethyl fumarate, ($c_a + c_s$) = 6.50×10^{-3} M.

Discussion

From comparison of the heteroconjugation constants with chloride of monomethyl glutarate (HE), glutaric and (H$_2$A), and butyric (HA) acid and considering inductive effects to be negligible, it is concluded that the monoester and the diacid are not intramolecularly hydrogen bonded in AN. Under these conditions and on statistical grounds $K^f(H_2A \cdot Cl^-) = 2K^f(HE \cdot Cl^-) = 2K^f(HA \cdot Cl^-)$ and experimentally this has been verified. This lends further support to the validity of eq 1 as a quantitative expression for estimating the extent of intramolecular hydrogen bonding in the monoanion.

As expected on the basis of the poor hydrogen bond accepting and donating capacity of acetonitrile, considerable intramolecular hydrogen bonding in this solvent occurs in the monoanion acid $\overline{HA}^-$ in o-phthalic acid and the homologous series of oxalic acid. This is particularly true for the six- and seven-membered ring structures of intramolecularly hydrogen-bonded bimalonate and biphthalate, respectively. With increasing chain length the strength of this bond in

Table I. Dissociation and Homoconjugation Constants of Diprotic Acids and Their Monoesters in Acetonitrile

Acid	pK_1	pK_2	$pK(HE)$[b]	$K_{homo}{}^f$	$K^f(HE_2^-)$	K' Eq 1[f]	K' Eq 5	$[\overline{H_3A_2}^-]/[H_3A_2^-]$	$K(\overline{H_3A_2}^-)$ eq 8
Oxalic	14.5_0	27.7		4×10^3 [e]					
Malonic	15.3	30.5	20.0[a]	0.9×10^3	7.5×10^3	2.5×10^4	1.6×10^1	1.5×10^3	0.9×10^3
Succinic	17.6_0	29.0	21.6	0.2×10^3	6.0×10^3	5×10^3	$5._6 \times 10^1$	9×10^1	0.2×10^3
Glutaric	19.2_0	29.9_5	22.2_6	0.6×10^3	6.2×10^3	6×10^2	$1._9 \times 10^1$	2×10^1	0.6×10^3
Adipic	20.3_5	26.9	22.2_4	1.4×10^3	4.7×10^3	4×10^1	5.7	5	1.2×10^3
Azelaic	20.9, 20.7_3[b]	24.8[b]	23.3[c]	2.7×10^3		1.2×10^1, 2×10^1 [b]	$2._5$[d]	5, $9._6$[b]	1.9×10^3 [d] 2.2×10^3 [b,d]
Fumaric	18.6[b]	22.9[b]	19.2		9×10^3	(2)			
o-Phthalic	14.3	29.8	20.0	0.9×10^2	10×10^3	3×10^5	$2._2 \times 10^2$	$1._4 \times 10^3$	0.9×10^2
Acetic	22.3			4.7×10^3					

[a] Monoethyl ester, all others monomethyl esters. [b] Found from paH of mixtures of monoester or diacid with tetramethyl or tetraethyl ammonium hydroxide in methanol; corrected for effect of methanol, see text. [c] pK(HE) assumed to be the same as pK_a of acetic acid. [d] $K(HE_2^-)$ assumed to be the same as homoconjugation constant of acetic acid. [e] Dihomoconjugate also formed, $K^f(2H_2A \cdot HA^-) = 2._0 \times 10^4$. [f] Recommended values.

Table II. Osmometric (DVP) Measurements in Solutions of Succinic Acid and Tetraethylammonium Bisuccinate in AN ($K_{homo} = 2.1 \times 10^2$, $K' = 5 \times 10^3$)
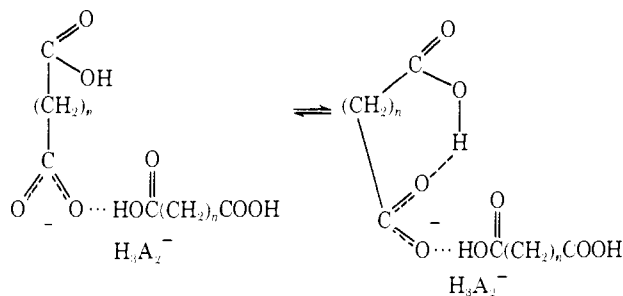
c_{H_2Suc}	c_{Et_4NHSuc}	$[H_2A]$	$\Sigma[HA^-]$	$\Sigma[H_3A_2^-]$	$m_{calcd}{}^a$	$m_{obsd}{}^a$
0	0.0129					0.0264
0	0.0200					0.0428
0.0103	0.0107	0.0049	0.0053	0.0054	0.0263	0.0282
0.0171	0.0179	0.0067	0.0075	0.0104	0.0425	0.0453
0.0295	0.0300	0.0095	0.0100	0.0200	0.0695	0.0700
0.0256	0.0364	0.0056	0.0164	0.0200	0.0784	0.0767
0.0408	0.0604	0.0064	0.0260	0.0344	0.12_7	0.118_3
0.0184	0.0392	0.0031	0.0239	0.0153	0.0815	0.0765

[a] Osmometric molarity.

the monoanion decreases as is evident from the decrease of K' (Table I). Even in azelaic acid K' was found to be as large as 12. The linear intramolecular hydrogen bond has maximum stability when O···H···O distance is 2.45 Å as concluded by McCoy[21] from K_1/K_{HE} values of 1,2-dicarboxylic acids in aqueous medium. This implies that the flexible chain in long-chained as well as in short-chained dicarboxylic acids must also be bent into a ring-accompanying formation of a stable intramolecular hydrogen bond in their monoanions. In unpublished work we have established that dimethyl sulfoxide and pyridine at concentrations less than 0.7 M do not affect the paH of bisuccinate-succinate mixtures. Therefore, these bases do not form a hydrogen bond with the intramolecularly bonded carboxylic group in $\overline{HA}^-$ and it is safe to conclude that the much weaker hydrogen bond acceptor water does not either. The stability of the intramolecular hydrogen bond in $\overline{HA}^-$ also accounts for the fact that osmometrically no indication of dimerization of the anion in dilute solutions of tetraethylammonium bisuccinate has been found (Table II). Additional evidence of the stability of the intramolecularly hydrogen-bonded monoanion species is derived from the value of the transfer activity coefficient $p^W\gamma^{AN}(\Sigma HA^-)$. From solubility data of succinic acid in water and AN (unpublished results) and K_1 values in these solvents, we derived a value of the transfer activity coefficient of bisuccinate, $p^W\gamma^{AN}(\Sigma HSuc^-) = +6.5$, while that for acetate, $p^W\gamma^{AN}(OAc^-) = +9.8$.[10] The difference between these two values is independent of the extrathermodynamic assumption employed for the estimation of transfer activity coefficients of these ions. In water the bisuccinate ion is present only as HA^- [4] which is stabilized by strong hydrogen bonding of the carboxylate ion and to a lesser extent of the carboxylic acid group with the solvent. If bisuccinate were not stabilized in AN by intramolecular hydrogen bonding, then a value of $p^W\gamma^{AN}(HSuc^-) \simeq p^W\gamma^{AN}(HOAc) + p^{W\cdot}\gamma^{AN}(OAc^-) = +0.4^6 + 9.8 = 10.2$ would be expected. The

difference between this value and the experimental value of $p^W\gamma^{AN}(\Sigma HA^-)$ is 3.7, and equal to log K' reported in Table I. The absence of homoconjugation between succinate and bisuccinate (Figure 3) cannot be attributed to increased stabilization of $\overline{HA}^-$ over HA^- because of coulombic repulsion between the mono- and dianions.

The carboxylate group in bisuccinate appears to be a strong hydrogen bond acceptor and forms heteroconjugates in AN with the hydrogen bond donors water and methanol. Since bisuccinate in AN is present practically entirely as $\overline{HSuc}^-$, the formation constant of the monohydrate of 5.0 found in the present work refers to that of $H_2O \cdot \overline{HSuc}^-$. It is reasonable to expect that the much stronger than water hydrogen bond donor succinic acid forms a relatively stable homoconjugate $\overline{HA}^- \cdots H_2A$. The two homoconjugates

$$
\text{(CH}_2)_n \text{ structure: } \quad O^{\diagdown} \!\!-\! O \cdots HOC(CH_2)_nCOOH \quad (H_3A_2^-) \quad \rightleftharpoons \quad O \cdots HOC(CH_2)_nCOOH \quad (\overline{H_3A_2}^-)
$$

$H_3A_2^-$ and $\overline{H_3A_2}^-$ are in equilibrium. The formation constant of $\overline{H_3A_2}^-$ is

$$K(\overline{H_3A_2}^-) = [\overline{H_3A_2}^-]/[\overline{HA}^-][H_2A] \tag{6}$$

and the overall homoconjugation constant, K_{homo}, is

$$K_{homo} = \frac{[\overline{H_3A_2}^-] + [H_3A_2^-]}{[H_2A]\{[\overline{HA}^-] + [HA^-]\}} \tag{7}$$

Substituting eq 1, 3, and 6 into eq 7 and considering $K(H_3A_2^-) = 2K(HE_2^-)$, eq 8 results. Using values of
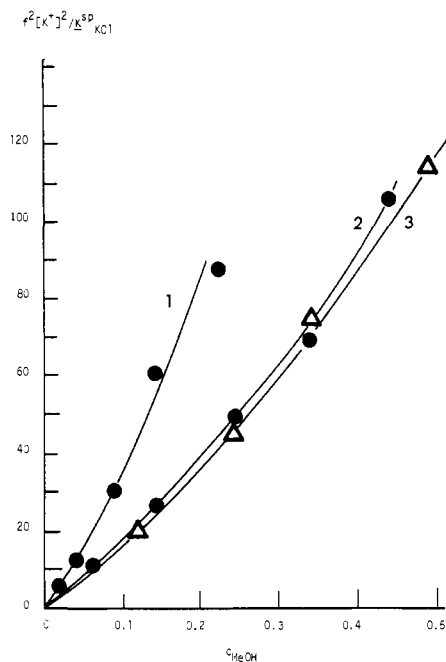
$f^2[K^+]^2/\underline{K}_{KCl}^{sp}$

Figure 6. Plots of $f^2[K^+]^2/K_{KCl}^{sp}$ vs. c_{MeOH} of potassium chloride for various acids: 1, glutaric acid; 2, monomethyl glutarate; and 3, butyric acid.

$$K_{homo} = (K(\overline{H_3A_2}^-)K' + 2K(HE_2^-))/(1 + K') \quad (8)$$

K_{homo}, $K(HE_2^-)$, and K' (from eq 1) reported in Table I, values of $K(\overline{H_3A_2}^-)$ are found from eq 8 and reported in the last column of Table I. These increase with increasing chain length as the strength of the intramolecular hydrogen bond decreases. The ratio of the two homoconjugate species $[\overline{H_3A_2}^-]/[H_3A_2^-]$, equal to $K'K(H_3A_2^-)/2K(HE_2^-)$, was calculated for the various acids and is also listed in Table I. This ratio decreases with increasing chain length considerably less than K' does, because $K(H_3A_2^-)$ increases, while $K(HE_2^-)$ is practically independent of the chain length. Finally, if it were assumed that only HA^- but not $\overline{HA}^-$ can homoconjugate, values of K' calculated from eq 5 are found which are much smaller than those from eq 1 (Table I).

On the basis of steric considerations it is expected that the bifumarate ion cannot be intramolecularly hydrogen bonded in AN. The value of log K' of 0.3 given in Table I is too close to zero to conclude the presence of $\overline{HA}^-$.

From the analytical viewpoint it is of interest to note that the intramolecular hydrogen bonding in $\overline{HA}^-$ to a large extent is responsible for the fact that in dipolar aprotic solvents, S, $(pK_2 - pK_1)_S$, denoted by $^2\Delta^1 pK_S$, is much greater than $(pK_2 - pK_1)_W = {}^2\Delta^1 pK_W$. The basic strength of $\overline{HA}^-$ is K' times smaller than that of HA^-. Consequently, K_1 must be K' greater and K_2 must be K' smaller than would be the case in absence of intramolecular hydrogen bonding. Thus $^2\Delta^1 pK_{AN}$ is expected to be at least of the order of 2 log K' units greater in AN than in water. Taking pK_1 and pK_2 values for succinic acid from Table I and literature values in water $^2\Delta^1 pK_{AN} - {}^2\Delta^1 pK_W = 11.4 - 1.3 = 10.1$, as compared to 7.4 units for 2 log K'. The difference of $10.1 - 7.4 = 2.7$ units is accounted for by values of $p^W\gamma^{AN}(H_2A)$ and $p^W\gamma^{AN}(A^{2-})$. This is to be documented in a subsequent paper in which the various constants of diprotic acids will be compared in water and methanol on the one hand, with those in the dipolar aprotic solvents acetonitrile and dimethyl sulfoxide on the other.

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