Protonation in Acetonitrile of Water, Alcohols, and Diethyl Ether[1]

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Abstract: The protonation in acetonitrile (AN) of the bases (B) water, alcohols, and diethyl ether has been studied by determining spectrophotometrically with Hammett indicators and dibromothymolbenzein their interaction with the solvated proton. Water forms the species BH^+, B_2H^+, B_3H^+, and B_4H^+; methanol and *n*-butyl alcohol yield only the first three, whereas *t*-butyl alcohol and diethyl ether yield the first two. The formation constants $K^f{}_{B_nH^+}$ of the various species have been determined and the values are reported in Table IV. Evidence has been presented that under our experimental conditions perchloric acid in the presence of water yields the hydrated proton and not the hydrolysis intermediate of AN, protonated acetamide. At small concentrations (0.01–0.1 *M*), *t*-butyl alcohol is a considerably stronger base than the other hydroxyl compounds. In 1 *M* solution *t*-butyl alcohol has the same basic strength as water. The formation constants $K^f{}_{Bz_I^-}$ and $K^f{}_{Bz_2I^-}$ of *o*-nitroaniline (I) with benzoate (Bz^-) have been calculated from the effect of I on the pa_H of mixtures containing a large excess of tetraethylammonium benzoate over benzoic acid. From the combined effect of I and water or methanol on the pa_H in these mixtures, it was concluded that I is not hydrated or methanolated in the concentration range used. Evidence has also been presented that IH^+ is not appreciably hydrated in AN. $pK^d{}_{IH^+}$ of *m*-nitroaniline in AN has been found equal to 7.6.

Upon addition of a base B to a solution of the strong acid, perchloric acid, in acetonitrile (AN), the solvated proton H_s^+ reacts with B with the formation of BH^+ and its homoconjugates, *viz.*

$$H_s^+ + B \rightleftharpoons BH^+ \qquad K^f{}_{BH^+} = [BH^+]/[B][H^+]_s \tag{1}$$

$$H_s^+ + nB \rightleftharpoons B_nH^+ \qquad K^f{}_{B_nH^+} = [B_nH^+]/[B]^n[H^+]_s \tag{1a}$$

In the present paper the formation constants $K^f{}_{BH^+}$ through $K^f{}_{B_nH^+}$ have been determined using as bases water, methanol, *n*- and *t*-butyl alcohols, and diethyl ether. It is well known that AN can be hydrolyzed with the formation of the intermediate, acetamide, and that this reaction is catalyzed by hydrogen ions. In order to be sure that under our experimental conditions we were dealing with the protonated forms of water, we have determined the acid dissociation constant, $K^d{}_{BH^+}$, of acetamide.

The ratios $[IH^+]/[I]$ of the Hammett indicators *o*-nitro-, *o*-nitro-*p*-chloro-, and *m*-nitroaniline and the uncharged indicator base dibromothymolbenzein (BrTBz) in solutions of perchloric acid in the presence of the above bases were determined spectrophotometrically.

In addition experiments have been designed to find whether the acid and basic forms of *o*-nitroaniline are associated with the base B (*e.g.*, hydrated or alcoholated), *viz.*

$$I + B \rightleftharpoons I_B \qquad K^f{}_{I_B} \rightleftharpoons [I]_B/[I][B] \tag{2}$$

$$IH^+ + B \rightleftharpoons IH_B^+ \qquad K^f{}_{IH_B^+} = [IH^+]_B/[IH^+][B] \tag{3}$$

In eq 2 and 3 I and IH^+ denote the indicator forms in pure AN.

In solutions of perchloric acid, the analytical concentration of the indicator, C_I, is given by

$$C_I = [I] + [IH^+] + [I]_B + [IH^+]_B \tag{4}$$

In dilute solutions ($\leq$0.01 *M*) of perchloric acid,[2] the salts $BH^+ClO_4^-$, $B_nH^+ClO_4^-$, and also $IH^+ClO_4^-$ and $IH_B^+ClO_4^-$ are considered to be completely dissociated in AN. The following electroneutrality rule then holds

$$[H^+]_s + [BH^+]\ldots[B_nH^+] + [IH^+] + [IH^+]_B = C_{HClO_4} \tag{5}$$

C_{HClO_4} denoting the analytical concentration of perchloric acid.

The formation constant of IH^+, $K^f{}_{IH^+}$, is defined as

$$K^f{}_{IH^+} = [IH^+]/[I][H^+]_s \tag{6}$$

Combining eq 1–6, eq 7 results

$$vy[H^+]_s{}^2K^f{}_{IH^+} + \{v(C_I - C_{HClO_4})K^f{}_{IH^+} + wy\}[H^+]_s - wC_{HClO_4} = 0 \tag{7}$$

where

$$v = 1 + K^f{}_{IH_B^+}[B]$$

$$w = 1 + K^f{}_{I_B}[B]$$

and

$$y = 1 + K^f{}_{BH^+}[B] + \ldots + K^f{}_{B_nH^+}[B]^n \tag{7a}$$

$K^f{}_{IH^+}$ in eq 7 is assumed to be unaffected by the presence of B.

When $C_I \ll C_{HClO_4}$, as applies when 1×10^{-4} *M* *o*-nitroaniline serves as a Hammett indicator in 2.10×10^{-3} *M* perchloric acid solution to which B is added, eq 7 reduces to

$$[H^+]_s = C_{HClO_4}/y \tag{7b}$$

Neglecting the formation of I_B and IH_B^+, $[H^+]_s$ is calculated from the experimentally determined ratio $[IH^+]/[I]$ using eq 6. Knowing $[H^+]_s$ the value of y is found directly from eq 7b. Determining y at various concentrations of B yields a set of simultaneous equations (eq 7a) from which the individual values of $K^f{}_{BH^+}$, ..., $K^f{}_{B_nH^+}$ can be found by a series of successive approximations or by the aid of a computer.

An estimation of the hydration and methanolation constants of I and hydration of IH^+ of *o*-nitroaniline was made in the following ways. Consider first the hydration of I. I is a hydrogen bond donor and it can associate with the benzoate ion, like water does.[3]

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[1] Acknowledgment is made to Air Force AFOSR Grant No. 1223-67.

[2] W. Muney and J. F. Coetzee, *J. Phys. Chem.*, **66**, 89 (1962).

$$\mathrm{I} + \mathrm{Bz}^- \rightleftharpoons \mathrm{Bz_I}^- \qquad K^{\mathrm{f}}{}_{\mathrm{Bz_I}^-} = [\mathrm{Bz_I}^-]/[\mathrm{I}][\mathrm{Bz}^-]$$

$$2\mathrm{I} + \mathrm{Bz}^- \rightleftharpoons \mathrm{Bz_{2I}}^- \qquad K^{\mathrm{f}}{}_{\mathrm{Bz_{2I}}^-} = [\mathrm{Bz_{2I}}^-]/[\mathrm{I}]^2[\mathrm{Bz}^-]$$

The following expression relates a_{H^+} in a mixture of benzoic acid (HBz) and its tetraalkylammonium salt in the presence of I, taking into account homoconjugation of HBz[3]

$$f^2a_{\mathrm{H}^+}{}^2c_{\mathrm{s}} - fVK^{\mathrm{d}}{}_{\mathrm{HBz}}a_{\mathrm{H}^+}\{(c_{\mathrm{a}} + c_{\mathrm{s}}) + K^{\mathrm{f}}{}_{\mathrm{HBz_2}^-} \times (c_{\mathrm{s}} - c_{\mathrm{a}})^2/V\} + V^2K^{\mathrm{d}}{}_{\mathrm{HBz}}c_{\mathrm{a}} = 0 \quad (8)$$

In eq 8, c_{a} and c_{s} represent the analytical benzoic acid and benzoate concentrations, respectively, while V as defined previously[3] for water ($\mathrm{I} = \mathrm{H_2O}$) is

$$V = 1 + K^{\mathrm{f}}{}_{\mathrm{Bz_I}^-}[\mathrm{I}] + K^{\mathrm{f}}{}_{\mathrm{Bz_{2I}}^-}[\mathrm{I}]^2 + \ldots$$

The benzoate ion has been found to form mono-, di-, and trihydrates[3] and in the present paper mono- and dimethanolates. When I and another hydrogen-bond donor such as water are present in the benzoic acid–benzoate mixture, the decrease in pa_{H} is attributed to association of the benzoate ion with water and I. V_{T} is then substituted for V in eq 8 where

$$V_{\mathrm{T}} = V + K^{\mathrm{f}}{}_{\mathrm{Bz_W}^-}[\mathrm{H_2O}] + K^{\mathrm{f}}{}_{\mathrm{Bz_{2W}}^-}[\mathrm{H_2O}]^2 + K^{\mathrm{f}}{}_{\mathrm{Bz_{3W}}^-}[\mathrm{H_2O}]^3$$

The expression for V_{T} is derived from the electroneutrality condition

$$c_{\mathrm{s}} = [\mathrm{Bz}^-] + [\mathrm{HBz_2}^-] + [\mathrm{Bz_I}^-] + [\mathrm{Bz_{2I}}^-] + [\mathrm{Bz_W}^-] + [\mathrm{Bz_{2W}}^-] + [\mathrm{Bz_{3W}}^-]$$

in benzoic acid–benzoate mixtures containing I and water in a similar way as when only one hydrogen-bond donor is present.[3] When no hydration of I occurs, the analytical concentrations of I and $\mathrm{H_2O}$ may be taken equal to their equilibrium concentrations in the expressions of V and V_{T} when both I and water are in large excess over benzoate. When hydration of I occurs, [I] and [$\mathrm{H_2O}$] can be much less than their analytical concentrations, the effect of a mixture of I and water upon the pa_{H} of the above benzoate mixture being less than that when I is not hydrated. When I is monohydrated, [I], [$\mathrm{H_2O}$], and [$\mathrm{I_W}$], equal to $C_{\mathrm{I}} - x$, $C_{\mathrm{H_2O}} - x$, and x, respectively, are calculated using the formation constant $K^{\mathrm{f}}{}_{\mathrm{I_W}}$ (*cf.* eq 2, $\mathrm{H_2O} = \mathrm{B}$).

Knowing [I] and [$\mathrm{H_2O}$], V_{T} is then calculated from the above expression for V_{T} and substituted in eq 8 to calculate the pa_{H} of the benzoate mixture.[3] Similar relations hold when methanol instead of water is used.

An indirect method was used to ascertain whether IH^+ of *o*-nitro- and *o*-nitro-*p*-chloroaniline are hydrated. In a previous study,[4] evidence was presented that neither the acid nor the basic forms of thymolbenzein are hydrated since $\mathrm{p}K^{\mathrm{d}}{}_{\mathrm{IH}^+}$ (red-yellow), equal to 9.85, as found in picrate buffers, is unaffected by water to at least 0.35 *M*.

It is reasonable to assume that the same holds true for the structurally related acid and basic forms of dibromothymolbenzein and *p*-naphtholbenzein used in the present study as indicators in the nitroaniline–perchloric acid buffers.

When both I and IH^+ are hydrated, the spectra of the hydrated and unhydrated forms being the same and $K^{\mathrm{f}}{}_{\mathrm{I_W}} = K^{\mathrm{f}}{}_{\mathrm{IH_W}^+}$, a constancy in $K^{\mathrm{f}}{}_{\mathrm{IH}^+}$ is obtained. This situation, however, is highly improbable.

Values of pa_{H} in mixtures of perchloric acid with an excess of *o*-nitro- or *o*-nitro-*p*-chloroaniline at various concentrations of water were calculated from the spectrophotometrically determined ratio of the acidic to basic forms of dibromothymolbenzein and *p*-naphtholbenzein. The pa_{H} values of the mixtures were also calculated using eq 7, taking $v = w = 1$ and using the hydration constants of the proton derived from spectrophotometric data in nitroaniline solutions containing a large *excess* of perchloric acid over I. Agreement between the calculated and experimental pa_{H} values indicates that the nitroanilinium ion is not or not appreciably hydrated. It is assumed that the nitroanilinium ion is not alcoholated.

Experimental Section

Chemicals. Acetonitrile was purified and dispensed as described previously.[5] The water content of the solvent was 2×10^{-3} *M* as determined by Karl Fischer titration. Perchloric acid "monohydrate" (actually $\mathrm{HClO_4 \cdot 1.37H_2O}$) was used as previously.[6] Perchloric acid "dihydrate" (70% $\mathrm{HClO_4}$ by weight) was Mallinckrodt Reagent Grade product. A freshly prepared 0.05 *M* stock solution of the "dihydrate" in AN was used in the study of the effect of water on the pa_{H} of perchloric acid solutions in AN using nitroanilines as indicator. In all other experiments involving perchloric acid, the "monohydrate" was used. Stock solutions in AN of 0.01–0.05 *M* of the "monohydrate" were standardized by visual titration with triethylamine using *p*-naphtholbenzein as indicator,[6] while those of the "dihydrate" were standardized by flooding 1 volume of an aliquot with 20 volumes of water and titrating with standard sodium hydroxide using phenolphthalein as indicator.

Benzoic acid,[7] tetraethylammonium benzoate,[7] *o*-nitro- and *o*-nitro-*p*-chloroaniline,[5] dibromothymolbenzein[4] (BrTBz), and *p*-naphtholbenzein[8] (*p*-NBz) have been used previously.

***m*-Nitroaniline.** Eastman Kodak White Label product was recrystallized from ethanol and dried *in vacuo* at 60°, mp 111° (lit.[9] 111.8°).

Acetamide, of unknown origin, was recrystallized from chloroform and dried *in vacuo* at 55° for 24 hr. **Methanol** and ***n*-butyl alcohol** were products used previously.[3] ***t*-Butyl alcohol** was Eastman Kodak White Label product. It was dried over molecular sieve 4A (Fisher Co.) and distilled at atmospheric pressure, bp 82° (lit.[9] 82.8°). The water contents of the purified alcohols were not determined. Mallinckrodt Analytical Reagent diethyl ether ("anhydrous") was used without further purification. The water content by Karl Fischer titration was 0.01% by weight. In studies of the protonation of ether, the effect of the water introduced from the ether was neglected.

Spectrophotometry. All absorption spectra were recorded with a Cary Model 15 spectrophotometer, while absorbance measurements were made with a Beckman DU spectrophotometer. In all spectrophotometric studies 1-cm and 1.0-mm stoppered silica cells were used except in those of the hydration of the proton with nitroanilines as indicator where 1.8-cm glass-stoppered Pyrex cylindrical cells were employed. Measurements were made immediately after preparation of the mixtures.

Potentiometry. Details of the potentiometric technique have been described elsewhere.[10] A Coleman tripurpose Catalog No. 3-472 glass electrode was used for all pa_{H} measurements.

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(6) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *Anal. Chem.*, **39**, 1627 (1967).

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(10) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **87**, 4428 (1965).

Results

Hydration and Methanolation of Uncharged *o*-Nitroaniline. Potentiometric pa_{H} data in a mixture of 3.00×10^{-3} *M* benzoic acid and 3.05×10^{-2} *M* tetraethylammonium benzoate containing from 0 to 1.03 *M* *o*-nitroaniline are presented in Table I. The experimental data can best be fitted[3] taking values of 5.0 and 6.8 for $K^{\mathrm{f}}_{\mathrm{Bz}_{I}^{-}}$ and $K^{\mathrm{f}}_{\mathrm{Bz}_{2I}^{-}}$, respectively (last column in Table I). Potentiometric data in the above benzoate mixture containing 1.03 *M* *o*-nitroaniline to which 0–1.26 *M* water or 0–1.25 *M* methanol was added are also presented in Table I. Calculated values of pa_{H} of these solutions using eq 8 and the expression for V_{T} and the previously reported constants $K^{\mathrm{f}}_{\mathrm{Bz_W}^{-}} = 2.3$,[3] $K^{\mathrm{f}}_{\mathrm{Bz_{2W}}^{-}} = 15.2$,[3] $K^{\mathrm{f}}_{\mathrm{Bz_{3W}}^{-}} = 10.2$,[3] $K_{\mathrm{HBz_2}^{-}} = 4.0 \times 10^{3}$,[7] $\mathrm{p}K^{\mathrm{d}}_{\mathrm{HBz}} = 20.7$,[7] and the above values of $K^{\mathrm{f}}_{\mathrm{Bz}_{I}^{-}}$ and $K^{\mathrm{f}}_{\mathrm{Bz}_{2I}^{-}}$ are also entered in Table I. From the previously reported effect of methanol on the pa_{H} of the above benzoate mixture,[3] the benzoate ion was found to associate with one and two molecules, respectively, of methanol, $K^{\mathrm{f}}_{\mathrm{Bz_{MeOH}}^{-}}$ and $K^{\mathrm{f}}_{\mathrm{Bz_{2MeOH}}^{-}}$ being 8.5 and 2.3×10^{1}, respectively. Good agreement between experimental and calculated pa_{H} values in Table I was obtained only with $K^{\mathrm{f}}_{\mathrm{I_B}} = 0$, indicating that *o*-nitroaniline is neither hydrated nor methanolated.

Table I. Effect of *o*-Nitroaniline (I) and Water or Methanol on the pa_{H} of Benzoic Acid–Tetraethylammonium Benzoate Mixture

Water added				Methanol added		
C_{I}, *M*	$C_{\mathrm{H_2O}}$, *M*	pa_{H} Obsd	pa_{H} Calcd	C_{MeOH}, *M*	pa_{H} Calcd	pa_{H} Obsd
3.00×10^{-3} *M* HBz, 3.05×10^{-2} *M* $\mathrm{Et_4NBz}$, $f = 0.66$						
0	0	23.67	23.67			
0.13	0	23.16	23.16			
0.29	0	22.63	22.72			
0.50	0	22.22	22.25			
0.79	0	21.80	21.77			
1.03	0	21.50	21.50			
1.03	0.13	21.38	21.44	0.25	21.28	21.16
1.03	0.25	21.24	21.37	0.496	21.02	20.81
1.03	0.47	20.97	21.19	0.74	20.78	20.66
1.03	0.72	20.70	20.91	1.00	20.53	20.40
1.03	0.96	20.44	20.66	1.25	20.33	20.25
1.03	1.26	20.21	20.31			
7.76×10^{-2} *M* HBz, 3.00×10^{-3} *M* $\mathrm{Et_4NBz}$, $f = 0.83$						
0	0	16.82				
0.09	0	16.73				
0.25	0	16.70				
0.55	0	16.60				
0.87	0	16.50				
0.87	0.55	16.55				
0.87	1.12	16.55				

Potentiometric pa_{H} data in 7.76×10^{-2} *M* benzoic acid and 3.00×10^{-3} *M* tetraethylammonium benzoate solutions to which up to 0.87 *M* *o*-nitroaniline had been added are also presented in Table I. Since the pa_{H}, in fact, decreases when *o*-nitroaniline is added, it is safe to conclude that *o*-nitroaniline does not associate with benzoic acid to any appreciable extent. Virtually no change in pa_{H} is found when water is added to this benzoate mixture containing 0.87 *M* *o*-nitroaniline.

Hydration of *o*-Nitro- and *o*-Nitro-*p*-chloroanilinium Ions. The effect of water on the pa_{H} of mixtures containing an excess of *o*-nitro-*p*-chloroaniline (*o*-N-*p*-ClA) or *o*-nitroaniline (*o*-NA) over perchloric acid was determined spectrophotometrically with dibromothymolbenzein and *p*-naphtholbenzein as indicators. The results are entered in Table II. The concentration of the acid form of the benzeins was determined at 550 and 625 mμ, respectively. At these wavelengths the absorbances of the uncharged nitroanilines, of the nitroanilinium ions, and of the basic form of the benzein indicators are negligible (see Figures 1 and 2). The spectra of the acidic form of the benzeins in the above nitroaniline buffers have the same shape in the presence as in the absence of water (Figures 1 and 2).

Table II. Effect of Water on pa_{H} of Mixtures of *o*-Nitro- (*o*-NA) and *o*-Nitro-*p*-chloroaniline (*o*-N-*p*-ClA)

			pa_{H}	
$m_{\mathrm{H_2O}}$	A_{550}	$[\mathrm{IH^+}]/[\mathrm{I}]$	Obsd	Calcd
0.0186 *M* *o*-N-*p*-ClA–0.00986 *M* $\mathrm{HClO_4}$, 1.33×10^{-5} *M* BrTBz as Indicator				
0.21	0.690	10.6	4.99	5.00
0.39	0.500	1.96	5.76	5.70
0.49	0.385	1.04	6.03	6.03
0.57	0.287	0.61	6.26	6.16
0.68	0.214	0.39	6.45	6.36
0.84	0.125	0.20	6.75	6.58
0.0344 *M* *o*-NA–0.00420 *M* $\mathrm{HClO_4}$, 2.12×10^{-5} *M* *p*-NBz as Indicator				
	A_{625}			
0	0.590	8.40	5.81	5.72
0.194	0.570	6.33	5.96	5.80
0.38	0.508	3.34	6.29	6.10
0.565	0.417	1.71	6.63	6.48
0.75	0.320	0.94	6.94	6.77
0.93	0.232	0.54	7.31	7.04
1.10	0.167	0.34	7.48	7.20

With the aid of eq 7, pa_{H} values of the mixture 0.0186 *M* in *o*-nitroaniline and 0.00986 *M* in perchloric acid, to which up to 1.0 *M* water was added, were calculated using the previously reported values of $K^{\mathrm{f}}_{\mathrm{IH}^{+}}$ of *o*-N-*p*-ClA, *o*-NA, BrTBz, and *p*-NBz equal to 3.88,[5] 4.85,[5] 5.9,[4] and 6.8,[3] respectively, and the hydration constants of the proton in Table IV. Satisfactory agreement between the experimental and calculated pa_{H} values presented in Table II was obtained taking $K^{\mathrm{f}}_{\mathrm{IH_W}^{+}}$ and $K^{\mathrm{f}}_{\mathrm{I_W}} = 0$, indicating that $\mathrm{IH^+}$ is not hydrated. The alcohols and diethyl ether are assumed not to associate with $\mathrm{IH^+}$.

Although the glass electrode yields good results in water-free mixtures containing excess of *o*-nitroaniline over its perchlorate, it yields erroneous values in the presence of water in these mixtures. For example, in the mixture 0.0344 *M* in *o*-nitroaniline and 0.00420 *M* in perchloric acid, the glass electrode yielded pa_{H} values 0.34, 0.40, 0.66, and 0.80 unit greater than the spectrophotometric values at water concentrations of 0.1, 0.2, 0.5, and 0.9 *M*, respectively.

Protonation of Acetamide. Standard perchloric acid in acetic acid, the reagent used in previous work for a similar purpose,[6] was added to a 0.0116 *M* solution of acetamide, and the pa_{H} was determined spectrophotometrically using 1.35×10^{-5} *M* dibromothymolbenzein as indicator. Ten mixtures were used varying in composition from 0.010 *M* B and 1.7×10^{-3} *M* $\mathrm{BH^+}$ at one extreme to 3.3×10^{-3} *M* B and 8.3×10^{-3} *M*

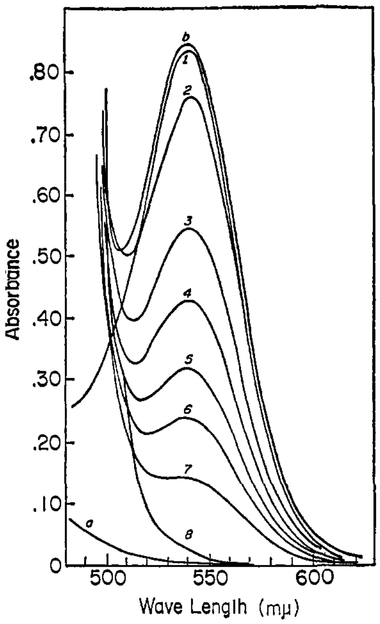

Figure 1. Spectra of 1.35 × 10^{-5} M dibromothymolbenzein in a mixture of 1.86 × 10^{-2} M *o*-nitro-*p*-chloroaniline and 9.9 × 10^{-3} M perchloric acid in the presence of water: (1) no water added, (2) 0.21 M H_2O, (3) 0.39 M H_2O, (4) 0.49 M H_2O, (5) 0.57 M H_2O, (6) 0.68 M H_2O, (7) 0.84 M H_2O, and (8) 5.5 M H_2O; (a) 1.35 × 10^{-5} M BrTBz in AN, (b) 1.35 × 10^{-5} M BrTBz in 0.001 M perchloric acid in AN (1-cm cell).

BH^+. An average value of $pK^d_{BH^+}$ was found equal to 6.05 ± 0.10.

Hydration of the Proton. The spectrum of 1.65 × 10^{-4} M *o*-nitroaniline in AN from 310 to 460 mμ in the presence of 1.5 M water is identical with that in the anhydrous solvent. However, the absorption at longer wavelengths increases with concentration of water. In a 0.0165 M *o*-nitroaniline acid-free solution absorbances were found at 494 mμ in a 1.00-cm cell at the following concentrations of water: no water present, 0.390; 0.37 M, 0.408; 0.90 M, 0.465; 1.25 M, 0.502; 1.78 M, 0.565; and 2.62 M water, 0.662. This effect apparently is not due to hydration of the indicator base.

The location of the maximum at 410 mμ and the general shape of the spectrum of 1.65 × 10^{-4} M *o*-nitroaniline from 310 to 460 mμ in presence of 2.0 M water and 0.27 M perchloric acid are the same as those in acid-free solvent.

Values of $[IH^+]/[I]$ were determined of nitroaniline indicators at concentrations ranging from 9 × 10^{-5} to 2.9 × 10^{-4} M in 5 × 10^{-4} to 1.4 × 10^{-2} M perchloric acid solutions containing up to 4.6 M water. Values of y were calculated from the ratio $[IH^+]/[I]$ using eq 6 and 7b, considering neither I nor IH^+ to be hydrated. In the calculation of $[H^+]_s$ (eq 7b), the following values of $pK^d_{IH^+}$ have been reported previously:[5] *o*-nitro- and *o*-nitro-*p*-chloroaniline, 4.85 and 3.88, respectively. A value of $pK^d_{IH^+}$ equal to 7.60 for *m*-nitroaniline was derived from potentiometric and spectrophotometric data in mixtures of 5.65 × 10^{-3} M *m*-nitroaniline and 1.9–5.5 × 10^{-4} M perchloric acid entered in Table III.

In the calculation of the analytical concentration of water, C_B, the amount of water present in the solvent and that introduced with the perchloric acid was taken into account. When the concentration of perchloric acid, C_{HClO_4}, is not negligible as compared to that of B, $C_B > [B]$, as a fraction of B is present in its protonated form(s), hence

$$[B] = C_B - [BH^+] - \ldots - n[B_nH^+] = C_B - \sum_1^n[B_nH^+] \quad (9)$$

At water concentrations greater than 0.1 M, this correction becomes negligible, while at smaller concentrations of water their correction was applied in the calculation of the hydration constants of the proton in the following way. As a first approximation, assuming $C_B = [B]$, preliminary values of the hydration constants $K^f_{H_3O^+} \ldots K^f_{H_{4w}^+}$ were found from the experimental y *vs.* C_B plot (eq 7a). Neglecting $[IH^+]$ and $[IH^+]_B$ in eq 5, the value of $[H^+]_s + \sum_1^n[H^+]_{nB}$ is found and thereby the concentration of the individual hydrates

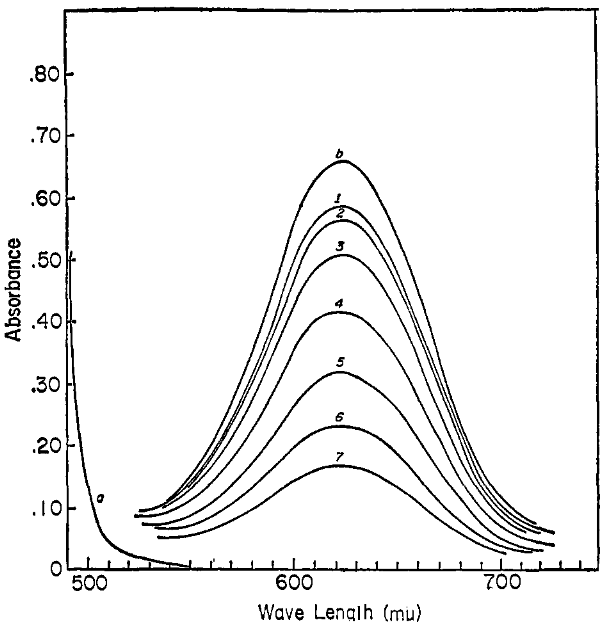

Figure. 2. Spectra of 2.12 × 10^{-5} M *p*-naphtholbenzein in mixtures of 3.44 × 10^{-2} M *o*-nitroaniline and 4.20 × 10^{-3} M perchloric acid in the presence of water: (1) no water added, (2) 0.194 M H_2O, (3) 0.38 M H_2O, (4) 0.56 M H_2O, (5) 0.75 M H_2O, (6) 0.93 M H_2O, and (7) 1.10 M H_2O; (a) 3.44 × 10^{-2} M *o*-NA in AN, (b) 2.12 × 10^{-5} M *p*-NBz in 6.5 × 10^{-3} M perchloric acid in AN (1-cm cell).

Table III. $K^d_{IH^+}$ of *m*-Nitroaniline from Potentiometric pa_H and Spectrophotometric $[IH^+]/[I]$ Values in Mixtures of I and $HClO_4$[a]

C_{HClO_4}, $M \times 10^3$	$[IH^+]/[I]$	pa_H	f	$pK^d_{IH^+}$[b]
0.19_5	0.036	9.09	0.97	7.6_4
0.390	0.074	8.75	0.93	7.5_9
0.780	0.16	8.48	0.91	7.6_4
1.38	0.32	8.15	0.88	7.6_0
2.15	0.61	7.90	0.85	7.6_1
2.77	0.96	7.72	0.83	7.6_2
3.60	1.7_5	7.43	0.81	7.5_7
4.15	2.7_7	7.24	0.80	7.5_8
4.80	5.6_5	6.95	0.78	7.5_9
5.48	32	6.36	0.77	7.7_4
				Av 7.6

[a] Total *m*-nitroaniline concentration, $[I] + [IH^+] = 5.65 \times 10^{-3}$ M. [b] $pK^d_{IH^+} = \log [IH^+]/[I] - \log f - pa_H$.

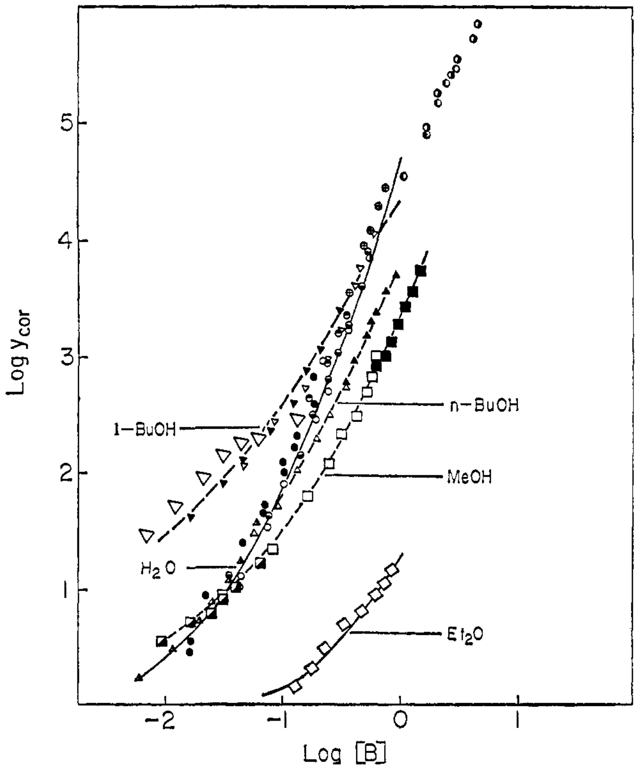

Figure 3. Plot of log y_{cor} *vs.* log [B] in perchloric acid solutions in AN. Water: ●, 8.6×10^{-5} *M* *o*-N-*p*-ClA; ◓, 1.33×10^{-4} *M* *o*-NA; ◑, 2.85×10^{-4} *M* *m*-NA–6.10×10^{-3} *M* $HClO_4$; ○, 6.95×10^{-5} *M* *o*-N-*p*-ClA, ◒, 1.00×10^{-4} *M* *o*-NA; ◐, 2.75×10^{-4} *M* *m*-NA–1.38×10^{-2} *M* $HClO_4$; ⊕, 1.7×10^{-5} *M* BrTBz–6.82×10^{-3} *M* $HClO_4$. Methanol: □, 1.2×10^{-4} *M* *o*-NA; ■, 1.75×10^{-5} *M* BrTBz–2.58×10^{-3} *M* $HClO_4$; ◪, 1.85×10^{-4} *M* *o*-N-*p*-ClA–5.15×10^{-4} *M* $HClO_4$. *n*-Butyl alcohol: △, 1.2×10^{-4} *M* *o*-NA; ▲, 1.75×10^{-5} *M* BrTBz–2.58×10^{-3} *M* $HClO_4$; ◭, 1.62×10^{-4} *M* *o*-N-*p*-ClA–6.00×10^{-4} *M* $HClO_4$. *t*-Butyl alcohol: ▽, 1.1×10^{-4} *M* *o*-NA–2.42×10^{-3} *M* $HClO_4$; ▽, 1.7×10^{-5} *M* BrTBz–2.32×10^{-3} *M* $HClO_4$; ▼, 1.7×10^{-5} *M* BrTBz–6.00×10^{-4} *M* $HClO_4$. Diethyl ether: ◇, 1.8×10^{-4} *M* *o*-N-*p*-ClA–2.58×10^{-3} *M* $HClO_4$. Drawn lines are calculated with the aid of $K^f{}_{B_nH^+}$ values in Table IV.

of the proton evaluated using the fractional forms (*cf.* eq 1 and 5).

$$[H^+]_{nW} = K^f{}_{H_nw^+}[H_2O]^n\left\{[H^+]_s + \sum_1^n[H^+]_{nW}\right\}\Bigg/\left(1 + \sum_1^n K^f{}_{H_nw^+}[H_2O]^n\right)$$

Substituting the values of $[H^+]_{nW}$ into eq 9, [B] is evaluated. Next, a plot of *y* *vs.* [B] is constructed and better values of the hydration constants are found and the cycle is repeated until constant values of $K^f{}_{H_nw^+}$ are obtained. A plot of experimental *y* values *vs.* the corrected values of $[H_2O]$ is presented in Figure 3. The hydration constants of the proton are listed in Table IV.

Table IV. Values of $K^f{}_{B_nH^+}$ for Water, Alcohols, and Ether in AN

B	$K^f{}_{BH^+}$	$K^f{}_{B_2H^+}$	$K^f{}_{B_3H^+}$	$K^f{}_{B_4H^+}$
Water	1.4×10^2	2.7×10^3	3.3×10^4	1.2×10^4
Methanol	2.3×10^2	1.4×10^3	8×10^2	0
n-Butyl alcohol	1.4×10^2	4.2×10^3	2.1×10^3	0
t-Butyl alcohol	2.7×10^3	1.7×10^4	0	0
Diethyl ether	1.5	2.1×10^1	0	0

Protonation of Alcohols and Diethyl Ether. Values of *y* and [B] (B = methanol, *n*- and *t*-butyl alcohols, and diethyl ether) were calculated as described above for water. In solutions in which C_B is small as compared to C_{HClO_4}, the water present in the solvent and that introduced with the perchloric acid must be taken into account. Equation 5 then becomes

$$[H^+]_s + [IH^+] + \sum_1^n[H^+]_{nW} + \sum_1^m[H^+]_{mROH} = C_{HClO_4} \quad (5a)$$

A correction for $\sum_1^n[H^+]_{nW}$ must be applied to *y* as obtained from eq 7b, *i.e.*

$$y_{cor} = y - \sum_1^n K^f{}_{H_nw^+}[H_2O]^n$$

$[H_2O]$ being taken as C_{H_2O}. This correction can be especially significant when diethyl ether, a very weak base, is used. As an example, $C_{HClO_4} = 2.58 \times 10^{-3}$ *M*, $C_{o\text{-N-}p\text{-ClA}} = 1.8 \times 10^{-4}$ *M*, $C_{Et_2O} = 0.17$ *M*, $y = 3.15$. Water introduced from solvent and perchloric acid ($HClO_4 \cdot 1.37H_2O$) = 0.003 + 0.0035 = 0.0065 *M*. Hence $y_{cor} = 3.15 - (1.4 \times 10^2)(6.5 \times 10^{-3}) - (2.7 \times 10^3)(6.5 \times 10^{-3})^2 = 3.15 - 1.0 = 2.1$. The species H_3w^+ and H_4w^+ are negligible. Whenever necessary, y_{cor} was also calculated in the experiments with alcohols.

Values of the protonation constants of the alcohols, methanol and *n*- and *t*-butyl alcohols, and of diethyl ether derived from the plots of y_{cor} *vs.* [B] in Figure 3 are tabulated in Table IV.

Discussion

The proton in AN is only weakly bonded to the solvent, H_s^+ being easily converted by weak bases, B, into B_nH^+. At very low concentrations of water or alcohol the unconjugated form BH^+ is the most stable protonated form. In preliminary work Kolthoff and Ikeda,[11] Coetzee and McGuire,[12] and Desbarres[13] considered only formation of H_3O^+ and reported at small water concentrations average values of $K^f{}_{H_3O^+}$ of 2.5×10^2, 1.7×10^2, and 3.1×10^2, respectively, in fair agreement with the value of 1.4×10^2 found in the present work.

It is of interest to note that the value of $K^f{}_{BH^+}$ in AN decreases in the order *t*-BuOH > MeOH > H_2O, *n*-BuOH ≫ Et_2O (Table IV) and that the same order is found in isopropyl alcohol as solvent.[14] The influences of the inductive and steric effects of the alkyl group adjacent to the oxygen atom in the alcohols upon the basicity of alcohols have been discussed by Wells,[15,16] who studied the protonation of alcohols in aqueous media.

In alcohol as solvent H_3O^+ is apparently the stable form at water concentrations up to at least 3 *M*. The reason undoubtedly is that H_3O^+ is hydrogen bonded to the alcohols, which are much stronger hydrogen-bond acceptors for H_3O^+ than AN. From the formation

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(11) I. M. Kolthoff and S. Ikeda, *J. Phys. Chem.*, **65**, 1020 (1961).
(12) J. F. Coetzee and D. McGuire, *ibid.*, **67**, 1810 (1963).
(13) J. Desbarres, *Bull. Soc. Chim. France*, 3240 (1965).
(14) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).
(15) C. F. Wells, *Trans. Faraday Soc.*, **61**, 2194 (1965).
(16) C. F. Wells, *ibid.*, **62**, 2815 (1966).

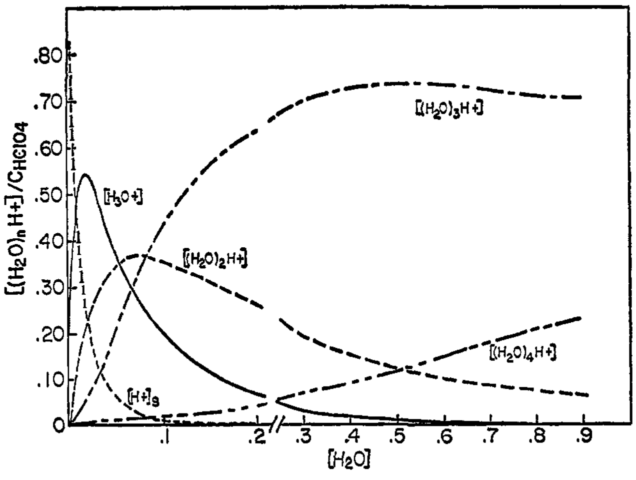


Figure 4. Plot of calculated values of $[(H_2O)_nH^+]/C_{HClO_4}$ vs. $[H_2O]$.

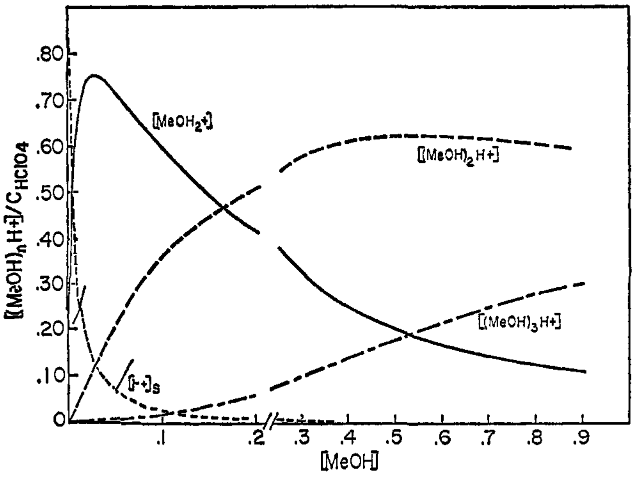


Figure 5. Plot of calculated values of $[(MeOH)_nH^+]/C_{HClO_4}$ vs. [MeOH].

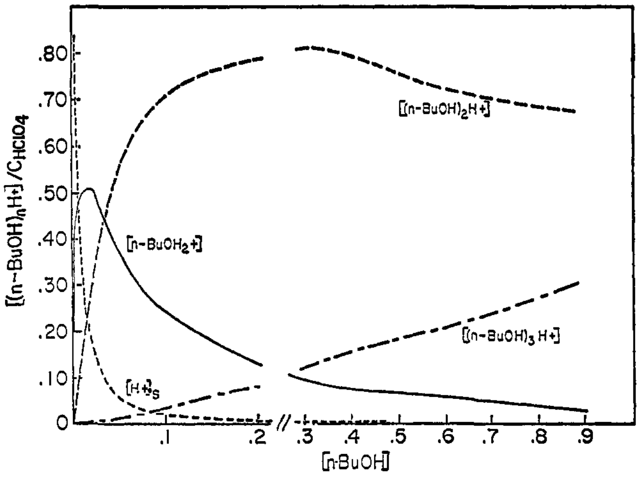


Figure 6. Plot of calculated values of $[(n\text{-}BuOH)_nH^+]$ vs. [*n*-BuOH].

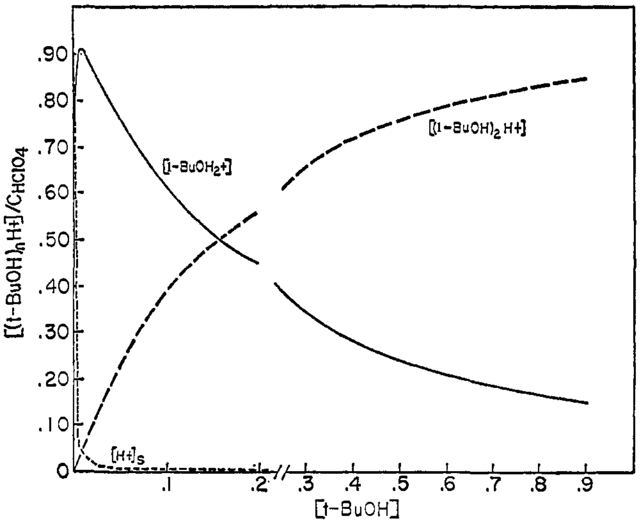
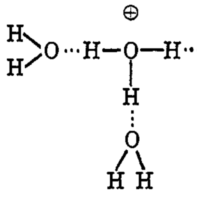


Figure 7. Plot of calculated values of $[(t\text{-}BuOH)_nH^+]$ vs. [*t*-BuOH).

constant, $K^f_{H_3O^+}$, in methanol and ethanol, it appears that water in these solvents is a considerably stronger base than the alcohols. Good agreement in the value of $K^f_{H_3O^+}$ in ethanol is found from kinetic methods (rate of hydrolysis of diethyl acetal[17] and ethylene oxide,[18] or esterification of aliphatic carboxylic acids[19,20]), from the effect of water on the conductance of weak acids,[17] and from spectrophotometric methods, $K^f_{H_3O^+}$ by these methods varying between 0.6 and 1.7×10^1. Also in methanol excellent agreement is found for the value of $K^f_{H_3O^+}$ derived from the kinetic[18] (4.8), conductometric[21] (4.3), and spectrophotometric[22] (4.3) methods.

It is evident from Figures 4–7 that with increasing concentration of B in acetonitrile as solvent, BH^+ is being converted into polyconjugates, the highest one with water being B_4H^+, with methanol and *n*-butyl alcohol being B_3H^+, and with diethyl ether being B_2H^+, as expected from the consideration of species constituted of each of the hydrogen atoms of the oxonium ion hydrogen bonded to the oxygen atom of B (structures **1–3**). In fact, the form $(H_2O)_4H^+$ is one of the most stable hydrates of the proton in water.[23] The fact that *t*-butyl alcohol forms only the mono- and dialcoholate in AN is attributed to steric effects as described by Wells in aqueous medium.[15,16] Unexplained is the fact that $(H_2O)_4H^+$ and $(ROH)_3H^+$ (ROH = methanol, *n*-butyl alcohol) are considerably less stable than the next lower hydrate or alcoholate (Table IV).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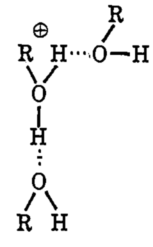
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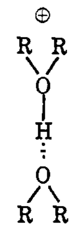
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It should be realized that an appreciable fraction of the proton is present as $(H_2O)_4H^+$ or $(ROH)_3H^+$ only at high concentrations of B, of the order of 1 *M* or greater (see Figures 4–6). At these high concentrations (1)

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(17) A. Deyrup, *J. Am. Chem. Soc.*, **56**, 60 (1934).
(18) C. Newall and A. Eastham, *Can. J. Chem.*, **39**, 1752 (1961).
(19) H. Goldschmidt and E. Sunde, *Ber.*, **39**, 711 (1906).
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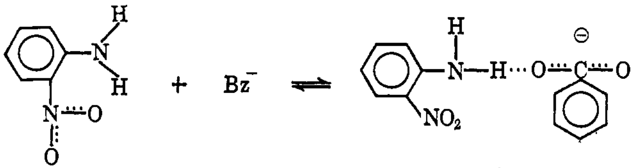
(23) See, *e.g.*, R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 83.

the activity of B may be less than the concentration, (2) part of B may be self-associated, (3) the value of p$K^{d}_{IH^+}$ may decrease as a consequence of change of the solvent character, and (4) there may be some hydrogen bonding of $(H_2O)_3H^+$ or $(ROH)_2H^+$ to AN. For these reasons the values of $K^{f}_{(H_2O)_4H^+}$ and $K^{f}_{(ROH)_3H^+}$ reported in Table IV may be smaller than the true values.

The basicity of water in AN is considerably less (Table IV) than that of acetamide, which has a p$K^{d}_{BH^+}$ of 6.0. Evidently acetamide is not formed under our experimental conditions because the decrease of H_s^+ would have been considerably greater than that plotted in Figure 4.

Quite generally the expression for basic strength can be quite ambiguous and may depend on experimental conditions, even in a given solvent. In acetonitrile the value of y is a better expression of basic strength than $K^{f}_{B_nH^+}$ even though y varies with concentration of B (Figure 3). For example, in 0.01 *M* solution y of *t*-butyl alcohol is some 10 times greater than that of water, but in 1 *M* solution y is about the same. Also in dimethyl sulfoxide water acts like a fairly strong base, $K^{f}_{H_3O^+}$ being 0.45.[24] On the other hand, in AN DMSO is a much stronger base than water, $K^{f}_{H^+DMSO}$ being 6.3×10^5 [25] as compared to $K^{f}_{H_3O^+} = 1.4 \times 10^2$.

o-Nitroaniline in its reactions with the benzoate ion behaves as a weak hydrogen-bond donor, the hydrogen-bond-donating properties possibly being weakened by intramolecular hydrogen bonding in structure **4**.



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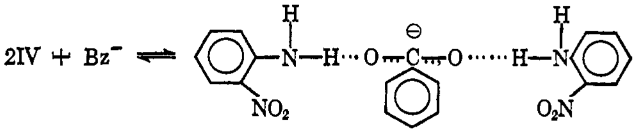

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Both in water and AN *m*-nitroaniline is a stronger base than the *ortho* isomer, the difference in their p$K^{d}_{BH^+}$ in AN being 7.6 (present paper) − 4.85 = 2.75 units, the same difference as in water.[26]

Although *o*-nitroaniline is a much stronger base than AN, water, and methanol, and therefore a much stronger hydrogen-bond acceptor than AN, no evidence has been obtained that it breaks the hydrogen bond between the donor water and the acceptor AN.

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The Radiolysis of Liquid *n*-Pentane

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Received November 13, 1967

Abstract: The radiation-induced decomposition of liquid *n*-pentane was studied as a function of temperature and total dose. Effects of olefins, oxygen, and nitrous oxide on product formation were also investigated. At room temperature, rupture between a primary and a secondary carbon atom occurs with a *G* value of 0.3 and between two secondary carbon atoms with a *G* value of 1.2. The total yield of C–C rupture was found to be temperature dependent, with *G* values of 1.7, 1.5, and 1.0 at temperatures of 95, 20, and −116°, respectively. Unsaturated products with six to ten C atoms, formed at low doses, are suggested to result from reactions within the spurs. Isomerization of radicals, though occurring, is relatively unimportant. Effects of an increase in radiation dose are attributed to the accumulation of olefins in the irradiated liquid. It is concluded that these olefins not only scavenge radicals and atoms, but that they are also involved in other processes. Similarly, the reduction in hydrogen yield in the presence of pentene is only partly due to scavenging of H atoms. Positive ions probably contribute to polymer formation in these solutions. Effects of oxygen and of nitrous oxide indicate that saturated products are mainly formed in reactions involving free radicals, whereas a considerable fraction of C_2–C_4 olefins are produced by molecular elimination. Positive ions are among the intermediates in the formation of these olefins.

The radiolysis of liquid *n*-pentane has been the subject of a number of investigations.[2–7] However, no complete product analysis has been reported at low radiation dose. Moreover, reported *G* values vary considerably. In this paper, results obtained in the radiolysis of liquid *n*-pentane, including the effects of temperature and radiation dose, are discussed. Experiments were also carried out in the presence of olefins and scavengers for radicals and electrons, notably oxygen and nitrous oxide.[8–12]

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