p-nitro groups are activating relative to hydrogen. In ethanol, which solvates anions strongly[4] and thus favors looser carbonium ion transition states like III, a *p*-methoxy substituent is more effective than a *p*-nitro substituent. In DMF, which solvates anions poorly,[4] but solvates polarizable solutes strongly, thus favoring a tight synchronous transition state like I, the *p*-nitro substituent is more effective than the *p*-methoxy substituent. Part of this effect may be due to solvation effects on the *p*-nitrobenzyl portion of the transition state, relative to the *p*-methoxybenzyl portion, in ethanol relative to DMF, but we feel that some of the solvent effect on the activating power of these substituents is due to differences of charge distribution at the actual reaction center.

Experimental Section

Materials. *trans*-1,2-Cyclohexyl dibromide[21] and cyclohexyl bromide,[22] 4-nitrobenzyl bromide,[22] and 4-methoxybenzyl bromide[19] were made by routine procedures. Other materials were commercial products and were dried, then purified by fractional distillation. All organic bromides analyzed for 100 ± 2% bromide in infinity samples of runs with excess base.

Kinetic Measurements. Reactions of azide ion were studied as in part XIV.[1] Reactions of sodium thiophenoxide were carried out under nitrogen in nitrogen-flushed solvents, using freshly prepared solutions. Thiophenoxide concentrations were estimated by titration with *p*-toluenesulfonic acid in ethanol, using brom phenol blue as indicator. Thiophenol was estimated by titration in ethanol with sodium methoxide in methanol, using thymol blue as indicator. Bromide ion was estimated by titration with silver nitrate in 10% sulfuric acid solution. Reactions of *t*-butyl bromide, benzyl bromide, and 4-methoxybenzyl bromide were poured into carbon tetrachloride and the electrolytes were extracted with water before estimation of thiophenoxide, azide, or bromide ion.[9] Solvolysis reactions were followed by estimation of hydrogen bromide as acid and as a source of bromide ion. Henry's law constants were measured to within ±25% as previously described.[1] Measurements with *t*-butyl bromide were performed without delay on fresh solutions to avoid solvolysis. Values for *t*-butyl chloride were similar, but our values are *ca.* 50% higher than those recorded by Winstein and Fainberg.[23] Uncertainties of this magnitude do not influence our discussion.

Reaction Products. Vpc analyses were made on a Perkin-Elmer 880 instrument with a flame ionization detector. Cyclohexene was estimated on a Porapak column at 180° and isobutylene was estimated on a 5% Ucon Polar 50-HB nonacid-washed Chromosorb W column at 30°. Propylene was not detected from reactions of isopropyl bromide with sodium thiophenoxide. The yields of olefin by vpc agreed with thiophenol produced as estimated by titration. A 2% yield of *t*-butyl phenyl thioether (n^{25}D 1.5325) was isolated[1] from the complete reaction of 0.07 *M* *t*-butyl bromide with 0.1 *M* sodium thiophenoxide in ethanol following de La Mare and Vernon.[10] The nmr spectrum of the thioether showed nine *t*-butyl protons at τ 8.72 (singlet) and five aromatic protons at τ 2.43–2.84. Acid was not produced and azide lost equalled bromide produced, confirming a substitution process for reactions of benzyl bromides with azide ion.

Acknowledgment. This work was supported by a grant from the Australian Research Grants Committee.

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The Protonation of Aromatic Carbonyl Compounds

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Contribution from the School of Chemical Sciences, University of East Anglia, Norwich, England. Received April 29, 1968

Abstract: The protonation behavior in aqueous sulfuric acid solution of various aromatic carbonyl compounds, together with mesityl oxide, has been investigated by uv spectrophotometry. The separation of protonation and medium effects on the spectra is discussed. Earlier conclusions on the protonation of these compounds are shown to be apparently in error, the increases in extent of proton take-up with increasing acidity being significantly greater than for a base following the H_A scale.

The pK_a values of aromatic carbonyl compounds have been the subject of extensive studies by Canadian workers,[2–5] and correlations of such pK_a's with MO calculations,[6] carbonyl stretching frequencies,[7] excited pK_a's by the Forster cycle,[8] Hammett σ^+ constants,[2,3,5,9] and hydrogen bonding[10,11] have been reported. Such determinations have often involved the assumption that these compounds are Hammett bases.[12] Since it has now been shown that protonation of amides[13,14] (which take up a proton at the oxygen site[15]), and of pyridine 1-oxides,[16] does not follow the H_0 acidity scale,[17–19] but generates a new acidity function, H_A, it might reasonably be postulated that oxygen protonations in general follow H_A. This contention receives support from the fact that both the

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Hammett H_0 scale[17] (which contains carbonyl compounds) and the H_0 scale derived for benzophenones,[9] which is arbitrarily anchored at 60% sulfuric acid, predict a smaller extent of protonation (*i.e.*, a smaller value of d(log I)/d(H_0), where log I = log [BH$^+$]/[B]) of the base members of these series than for the H_0 scale determined for primary anilines alone,[18,19] the H_A scale being the only distinct scale which postulates a smaller increase in extent of protonation with increasing acidity than H_0. Other workers also find evidence for slow protonation in the case of pyridones[20] and pyrimidinediones[21] benzaldehyde,[22] acetophenone,[22,23] benzoylbenzoic acids,[24] 1- and 2-naphthaldehydes and acetylnaphthalenes,[8] and aliphatic esters[25,26] (in the latter case, protonation is known to occur on the carbonyl oxygen[27]).

The purpose of this investigation was, therefore, to examine the protonation behavior in sulfuric acid, using the uv technique, of a set of aromatic carbonyl compounds, together with mesityl oxide, and thus to evaluate the adherence of these compounds to the H_A scale. Table I gives the H_0 (half-protonation) values (which only represent pK_a's if m(d(log I)/d(H_0) is unity) previously obtained for this set of compounds, together with m values, where available.

Table I. H_0 (Half-Protonation) Values Obtained by Previous Workers

Indicator	$-H_0$ (half-protonation)	m
Benzaldehyde	6.99[a]	
	7.10[b]	
	7.39[c]	0.82[c]
Acetophenone	6.03[d]	
	6.15[e]	
	6.45[c]	0.73[c]
	6.45[f]	0.52[f]
p-Methoxybenzaldehyde	5.54[b]	
Benzophenone	6.16[g]	
	6.18[h]	
	6.42[i]	0.57[i]
Fluorenone	6.6[g]	
Anthraquinone	8.37[j]	
Methyl benzoate	7.78[k]	
1-Acetylnaphthalene	5.86[a]	
	6.22[l]	0.83[l]
2-Acetylnaphthalene	6.04[a]	
	6.16[l]	0.86[l]
1-Naphthaldehyde	6.34[a]	
	6.63[l]	0.85[l]
2-Naphthaldehyde	6.68[a]	
	7.08[l]	0.84[l]
Mesityl oxide	4.0[m]	

[a] Reference 6. [b] Reference 5. [c] Reference 22. [d] Reference 31. [e] Reference 2. [f] Reference 23. [g] Reference 4. [h] A. Fisher, B. A. Grigor, J. Packer, and J. Vaughan, *J. Amer. Chem. Soc.*, **83**, 4208 (1961). [i] Reference 9, calculated by plotting log I *vs.* H_0.[18] [j] Reference 17. [k] Reference 12. [l] Reference 8. [m] Calculated approximately from ref 30.

Experimental Section

The carbonyl compounds were all available commercially. The liquid samples were distilled, usually under reduced pressure, and their purity was checked by refractive index determination and vpc. 2-Naphthaldehyde, 2-acetylnaphthalene, anthraquinone, benzophenone, and fluorenone were recrystallized and their purity checked by melting point.

The sulfuric acid solutions were made up as given previously.[28] The complete spectra were initially recorded on a Perkin-Elmer "Ultracord" Model 137 self-recording spectrophotometer, and then at certain wavelengths (see Table IV) on a Unicam SP500 spectrophotometer thermostated at 20°. These wavelengths were selected such that either the free base or conjugate acid species gave an absorption maximum, while the other had only a small absorption. In all cases solutions were measured as soon as possible after they had been made up in order to reduce the chance of decomposition. Reversibility of protonation was checked by dilution of a specimen solution of the conjugate acid, when spectra of the free base species were obtained.

The H_0 values of the solution used were those of Jorgenson and Hartter.[18] Sigmoid curves of optical density against H_0 were drawn in all cases, and care was taken that not only was the protonation region well defined by several points, but also the "arms" of the sigmoid curve. Table II gives the optical densities and H_0 values used for constructing these curves in the case of 1-acetylnaphthalene.[29] Figure 1 has typical curves showing that medium effects are often marked for both conjugate acid and free base peaks, and may vary from very small as in the case of fluorenone to very large, anthraquinone being the extreme example. In fact, the medium effect on anthraquinone was scarcely distinguishable from the protonation region, whereas in all other cases, the two regions were quite distinct. As noted by previous workers, the medium effect produced a variation of OD at a fixed wavelength which was linear with H_0.[28]

Table II. Optical Densities and Log I Values for 1-Acetylnaphthalene

H_2SO_4, %	$-H_0$	Free base peak (310 mμ) OD	Free base peak (310 mμ) Log I	Conjugate acid peak (422 mμ) OD	Conjugate acid peak (422 mμ) Log I
96.08	10.03	0.050		1.295	
92.98	9.48	0.074		1.250	
86.88	8.42	0.101		1.178	
82.30	7.70	0.136		1.150	
78.55	7.11	0.219	0.929	0.925	0.673
76.24	6.76	0.344	0.484	0.769	0.360
74.00	6.41	0.533	0.083	0.571	0.073
72.16	6.12	0.616	−0.032	0.450	−0.149
71.01	5.95	0.747	−0.265	0.402	−0.233
70.32	5.85	0.812	−0.299	0.347	−0.332
69.08	5.65	0.880	−0.505	0.269	−0.487
67.90	5.56	0.928	−0.604	0.234	−0.563
66.65	5.40	0.992	−0.757	0.178	−0.726
63.70	5.00	1.118		0.027	
59.28	4.40	1.298		0.012	
51.92	3.57	1.411		0.010	
H_0 (half-protonation)		−6.22	H_0 (half-protonation)	−6.28	
	m	0.87	m	0.81	

Results

The treatment of data such as given in Table II falls into two parts. The first is the calculation of meaningful log I values, and the second is the use of these log I values to obtain realistic thermodynamic pK_a values, *i.e.*, pK_a values which will be an accurate indication of the amount of conjugate acid present in dilute aqueous sulfuric acid in a region where H_0 and pH become equivalent.

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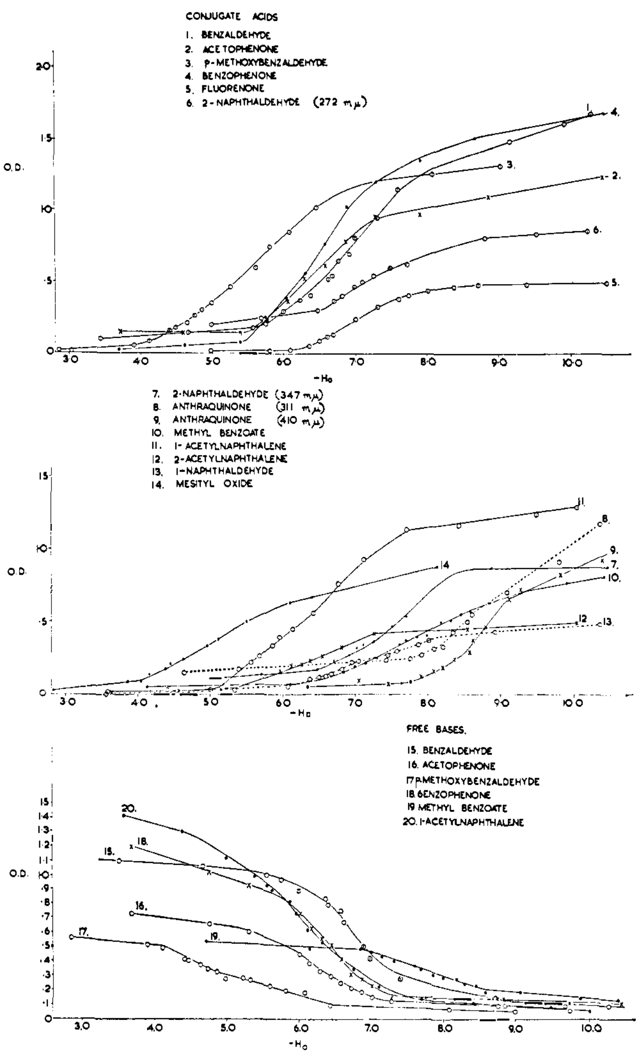

Figure 1. Protonation and medium effects on the uv absorption spectra of carbonyl compounds in sulfuric acid.

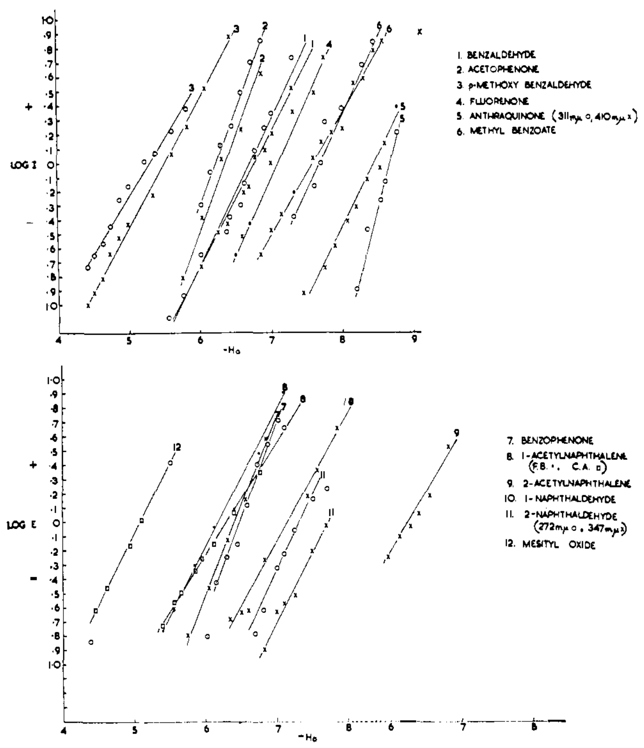

Figure 2. Log I against H_0 plots: free base, ⊙; conjugate acid, ×.

Both parts of the calculation involve assumptions, approximations, and errors which are present in all treatments, but in some are not immediately apparent. Accordingly, we discuss, in some detail, the various ways in which such estimations can be made.

Indicator Ratios. The factor which affects the determination of accurate log I values in aqueous sulfuric acid by uv measurement is the medium effect on the spectra, whereby both the intensity and position of peak maxima vary with acid concentration in regions where observable protonation is absent. This effect is marked for carbonyl compounds[30] (see Figure 1 and Table II), and methods of calculation which ignore this, where it is present, must lead to erroneous results. Indeed, even in the absence of medium effects, experimental log I values may well vary depending on the wavelength used for measurement.[19] For this reason, we have chosen wavelengths where the absorption of one species is at a maximum, and the other at a minimum. Various methods of compensation for the medium effect have been tried,[12,30–32] of which certainly the most accurate and involved is that of Reeves.[32] In these experiments we have utilized the method of Katritzky, Yates, and coworkers,[26,28] which has the virture of simplicity and appears to be reasonably reliable. The graphical form[28] of this correction was employed. The "arms" of the sigmoid curve were extended linearly and the appropriate OD relevant to the free base and conjugate acid read off for the given acidities and substituted in the standard formula $I = (\mathrm{OD_B} - \mathrm{OD})/(\mathrm{OD} - \mathrm{OD_{BH^+}})$. The log I values between +1.0 and −1.0 were thus calculated, and plotted against H_0 values (Figure 2). The resultant values of H_0 (half-protonation) and m are given in Table IV. Medium effects differ considerably for the conjugate acid and free base peaks of the same compound, and we have, therefore, in several cases taken readings at both peaks. The measure of agreement is in general reasonable, and we take it as an indication that this method of correction is adequate in these cases.

Our H_0 (half-protonation values, Table IV) are, with some exceptions, in good agreement with previous results (Table I), but the m values, unlike those of previous workers, are scattered about unity, showing that the postulate that such compounds follow H_A is erroneous. The discrepancy between our results and previous results may well be explained in terms of failure to account adequately for medium effects in the latter cases. For example, in the case of the conjugate acid peak of acetophenone, we have calculated log I values taking a fixed value for the optical density of the conjugate acid at 95.5% acid and the free base at 44%. This yields a value of m of 0.94. A similar calculation for the conjugate acid peak of benzaldehyde gives 0.82, and for benzophenone, 0.63.

pK_a Values. Methods for the determination of the pK_a values of weak bases from a knowledge of indicator ratios may be grouped into three distinct approaches.

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(31) L. A. Flexser, L. P. Hammett, and A. Dingwall, *J. Amer. Chem. Soc.*, **57**, 2103 (1935).

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(i) The log I values are plotted against the available acidity functions H_x, and the acidity function for which $d(\log I)/d(H_x)$ is approximately unity is utilized in the equation

$$H_x = pK_a - \log I \qquad (1)$$

(ii) The validity of the linearity of plots of H_x *vs.* H_0,[26] and their common intersection at approximately pH = H_0 = 0, is assumed, whence eq 2, 3, and 4 may be deduced

$$mH_0 = mH_0\,(\text{half-protonation}) - \log I \qquad (2)$$

$$pK_a = mH_0\,(\text{half-protonation}) \qquad (3)$$

$$\log I = -mH_0 + pK_a \qquad (4)$$

and thus

$$m \log f_{BH^+}/a_{H^+}f_B = \log f_{SH^+}/a_{H^+}f_S$$

where B is a Hammett base, and S is a base following the H_x acidity function. (iii) Bunnett's linear free energy relationship[33]

$$\log I - \log [H^+] = (\phi - 1)(H_0 + \log [H^+]) + pK_a \qquad (5)$$

may be employed, where $(\phi - 1)$ is an arbitrary choice of slope parameter.

Method i is usually only appropriate where the base under study is protonating on the same functional group as indicators used for establishing the scale. Errors arise from deviations of $d(\log I)/d(H_x)$ from unity, and also from errors built into the acidity scale itself. Thus the amide acidity scale appears to be anchored incorrectly (a conclusion which follows from the use of both eq 4 and 5), while others contain indicators for which plots of log I *vs.* per cent H_2SO_4 show poor parallelism in the overlapping regions (see in particular ref 18). Methods ii and iii appear mutually contradictory. Plots of log I *vs.* H_0 and log I − log [H+] *vs.* H_0 + log [H+] can only both be linear theoretically if H_0 *vs.* log [H+] is linear, which of course is not the case. However, both types of plot are in practice linear. This may be demonstrated for Bunnett's work by plotting H_x + log [H+] *vs.* H_0 + log [H+]. This implies, comparing (4) and (5), that

$$(\phi - 1)H_0 + \phi \log [H^+] = -mH_0 \qquad (6)$$

which apparently arises from the practical circumstance that the relations $(\phi - 1) \sim -m$ and $(\phi - 1)H_0 \gg \phi \log [H^+]$ are valid. This may be substantiated by comparing the average values of $(\phi - 1)$ and m for H_A, $(\phi - 1) = -0.62$, $m = 0.61$; H_0''', $(\phi - 1) = -1.38$, $m = 1.29$; H_R, $(\phi - 1) = -2.24$, $m = 2.05$; H_I, $(\phi - 1) = -1.43$, $m = 1.31$.

For the bases under study, we omitted the use of method i, because it is only valid if the bases follow known acidity functions. Method iii is more tedious to use than ii, and, as Table III shows, does not yield significantly different results (although we do not intend to imply that method ii is fundamentally more significant than iii[34]). Table III shows apparent pK_a values calculated by the latter two methods for a few bases arbitrarily selected from Bunnett's and Olsen's compilation,[33] showing that the two values approximate very closely.

Table III. Comparison of pK_a Values by (i) the Acidity Function, and the Methods of (ii) Yates and (iii) Bunnett

Compound	H_0[a]	m	pK_a values i	ii	iii
p-Methoxybenzamide	−1.67	0.69	−1.44	−1.15	−1.17
m-Nitrobenzamide	−3.30	0.57	−2.42	−1.88	−2.03
2,4-Dichloro-3,5-dinitrobenzamide	−5.68	0.55	−3.73	−3.12	−3.16
N,N-Dimethyl-2,4-dinitro-1-naphthylamine	−1.90	1.32	−2.59	−2.51	−2.34
N-Methyl-2,4-dinitrodiphenylamine	−4.71	1.34	−6.19	−6.31	−6.08
N,N-Dimethyl-2,4,6-trinitroaniline	−4.78	1.31	−6.55	−6.26	−6.30
2,3-Dimethylindole	−1.07	1.25	−1.49	−1.34	−1.35
Indole	−2.55	0.97		−2.47	−2.46
3-(Acetic acid)indole	−4.40	1.31	−6.13	−5.76	−5.76
5-Nitroindole	−5.47	0.82		−4.49	−4.61
4-Methoxytriphenylmethanol	−1.77	2.04	−3.40	−3.61	−3.73
3,3′,3′′-Trichlorotriphenylmethanol	−5.52	1.71	−11.03	−9.44	−9.14

[a] Half-protonation.

Table IV. pK_a Values of Carbonyl Compounds

Compound	Form	$-H_0$[b]	m	$-pK_a$	λ,[c] mμ
Benzaldehyde	B	6.74	1.02	6.87	258
	A	6.77	0.98	6.63	297
Acetophenone	B	6.21	1.26	7.82	252
	A	6.34	1.26	7.99	296
p-Methoxybenzaldehyde	B	5.28	0.81	4.28	285
	A	5.50	0.88	4.84	345
Benzophenone	B	6.48	1.30	8.42	257
	A	6.40	1.25	8.00	344
Fluorenone	A	7.04	1.16	8.17	402
Anthraquinone[a]	A	8.66	2.00		311
	A	8.48	1.00		410
Methyl benzoate	B	7.65	1.06	8.11	235
	A	7.57	0.86	6.51	263
1-Acetylnaphthalene	B	6.22	0.87	5.41	310
	A	6.28	0.81	5.09	422
2-Acetylnaphthalene	A	6.27	0.91	5.71	437
1-Naphthaldehyde	A	7.18	0.90	6.46	428
2-Naphthaldehyde	A	7.34	0.96	7.05	272
	A	7.73	0.91	7.03	347
Mesityl oxide	A	5.10	1.05	5.36	285

[a] Extremely large medium effect (see Figure 1); makes the significance of these results very slight. [b] B = free base, A = conjugate acid. [c] Wavelength for determination.

Table IV shows the pK_a values calculated for our carbonyl compounds using method ii.

Discussion

It is quite clear that the precise experimental definition of a thermodynamic pK_a value is only possible when the observable region of protonation falls well within the pH region where the equation pH = pK_a − log I is strictly obeyed. The determination of pK_a values outside this range for very weak or very strong bases is an inaccurate and arbitrary process. (Although for the determination of acidity functions for strong bases such as the anions of anilines and hydrocarbons, the parallelism of log I plots is much better, and medium

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(33) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899 (1966).

(34) See E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **86**, 2671 (1964), ref 20! This result was anticipated by Bunnett and Olsen. They found,[33] however, that their approach is more significant for treatment of kinetic data.

effects are generally absent. The H_- function is thus a good deal more comprehensive than its H_0 counterpart.[35,36])

We consider that the pK_a values given in Table IV are a better approximation to thermodynamic pK_a's than the H_0 (half-protonation) values also included in this table. This would not necessarily invalidate correlations of other parameters defining properties of such molecules with H_0 (half-protonation) values. Hence, previous correlations in the literature of these values with σ^+ for substituted benzaldehydes,[5] acetophenones,[2] and benzoic acids[3] are quite valid, provided the values of m are the same for all the bases considered, the m value in such cases being incorporated in ρ. In the same way, the correlation of σ with pK_a reported for substituted benzamides[37] is appropriate, even though later work showed these compounds to be following H_A; however, the ρ value is 0.78 (1.30 × 0.6) rather than 1.30. In this connection, however, we note from Table IV that the m value for benzaldehyde is substantially different from that for p-methoxybenzaldehyde; perhaps it is significant that the methoxy substituent gives a poor correlation in σ^+ plots.[2,3,5] In fact, experimental work on the various acidity functions has demonstrated that it is the functional group being protonated which decides the acidity function being followed, rather than the substituent adjacent to that particular function, usually attached *via* an aromatic nucleus. (Anomolous effects of the nitro group on solvation and hence acidity–activity coefficient variation behavior, the Hammett–Chapman effect, have been evaluated.[38,39] However, it appears that such effects will largely cancel since one is considering in any acidity function terms such as ($\log f_{BH^+} - \log f_B$). In any case, recent work suggests that the effect is small.[40])

Our results demonstrate that these compounds do not follow the H_A scale, and protonate more steeply than amide bases, with increasing acidity. Any acidity function H_x is defined by the equation $H_x = \log f_{BH^+}/a_{H^+}f_B$, and for a given set of bases to follow the same acidity function, the ratio f_{BH^+}/f_B must be the same at the same acidity. Attempts to define the change of f_{BH^+}/f_B with acidity in terms of specific hydration numbers[12] has been criticized,[41] but it appears reasonable to explain qualitatively the difference between the various scales (and therefore between m values) in terms of differing degrees of solvation, at a given acidity, of both the cationic and free base species of the various basic types.

The correlation of pK_a values with other physical properties of these molecules has already been indicated. An important aspect of these pK_a values would appear to be in the field of aromatic electrophilic substitution, where an accurate determination of rates of nuclear hydrogen exchange or nitration in such compounds, using solutions in concentrated sulfuric acid, requires a knowledge of accurate pK_a values and acidity function behavior. Such a program is in hand elsewhere;[42] it appears to represent an extension of the principles elucidated by Ridd, Schofield, and Katritzky, and coworkers, for the study of such reactions in heteroaromatic species.[43]

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(35) K. Bowden, *Chem. Rev.*, **66**, 119 (1966).

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Carbonium Ions. XXI. Protonated Cyclopropane[1]

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Abstract: Further evidence is obtained for the existence of protonated cyclopropane as a chemical species. Its stability is estimated to be intermediate between the isomeric 1-propyl and 2-propyl cations. In reactivity, it is unselective in alkylating toluene indicating high reactivity as an alkylating agent. In contrast, it is unable to abstract hydride from branched alkanes.

Protonated cyclopropane, c-$C_3H_7^+$, was proposed as an intermediate to explain the formation of cyclopropane from the nitrous acid deamination of propylamine.[3] Since then, a variety of observations have found explanations in terms of protonated cyclopropane intermediates.[4-10]

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(1) This work was supported by Grant GP-5663 from the National Science Foundation and Grant 2253-C from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is made for this support and to the donors of the Petroleum Research Fund.

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