reaction, the solution was heated at 180–190° for 1 hr. The solid product was recrystallized from ethanol–water to give 7.5 g. of colorless crystals, m.p. 179–180°.

Anal. Calcd. for $C_{11}H_{12}N_2O$: C, 70.2; H, 6.4; N, 14.9. Found: C, 70.1, 70.2; H, 6.6, 6.6; N, 15.0, 15.1.

5-Chloro-1,3-dimethyl-4-phenylpyrazole (**7b**).—A mixture of 6.5 g. of the pyrazolone **6b**, 5.4 g. of pyridine, and 9.5 g. of freshly distilled $POCl_3$ was heated for 40 hr. at 110–130° and was then poured onto ice. Twenty milliliters of 4 *N* NaOH was then added and the resulting oil was extracted with chloroform. After the chloroform extracts were washed with alkali and water and dryed over $MgSO_4$, the solvent was evaporated and the residue was distilled to give 3.0 g. (42%) of colorless oil, b.p. 100–104° (0.5 mm.) and 151–152° (15 mm.).

Anal. Calcd. for $C_{11}H_{11}ClN_2$: Cl 17.1. Found: C, 17.0, 17.1.

1,3-Dimethyl-4-phenylpyrazole (**8b**).—Hydrogenation of **7b** was carried in the same way described for **7a**. From 7.3 g. of **7b** was obtained 5.0 g. of crude pyrazole. Distillation gave a colorless oil, b.p. 150–152° (13 mm.). This material contained a trace of the chloropyrazole and was purified by conversion to the **picrate** which was recrystallized from ethanol, m.p. 148°.

Anal. Calcd. for $C_{17}H_{15}N_5O_7$: C, 50.87; H, 3.77; N, 17.45. Found: C, 50.42; H, 4.02; N, 16.80.

After decomposition of the picrate with warm NaOH solution, the base was extracted with ether; after standing over K_2CO_3 to remove traces of picric acid, the solution was evaporated and the pyrazole was distilled, b.p. 155–156° (15 mm.). The oil crystallized on standing, m.p. ~40°.

Anal. Calcd. for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 77.06; H, 7.29; N, 16.11.

Reaction of Methylhydrazine with 1-Ethoxymethylene-1-phenylacetone.—To a solution of 20 g. of the enol ether in 100 ml. of ethanol were added 10 g. of H_2SO_4 in 20 ml. of water and then a solution of 8.6 g. of methylhydrazine in 60 ml. of water. After refluxing for 1 hr. the ethanol was distilled and the residue was diluted with water. The solution was made alkaline and extracted with ether. The solution was dried and concentrated and the residue was distilled at 18 mm. to give 5 g. of yellow oil, b.p. 155–157°, and 8 g., b.p. 157–159°. Redistillation of the second fraction gave 7 g., b.p. 161–164° (19 mm.). This material contained about 65% of the 1,3-dimethyl isomer (**8b**) and 35% of the 1,5-dimethyl compound (**10b**) estimated from n.m.r. peak areas.

Methylation of 5-Methyl-4-phenylpyrazole.—To a solution of 5.5 g. of 5-methyl-4-phenyl-pyrazole[2] (**12**) in 50 ml. of ethanol was added a solution of 1 g. of sodium in 45 ml. of ethanol and 10 g. of methyl iodide. After standing for a day the solution was evaporated, water was added, and the pyrazole was extracted with ether. Distillation at 0.5 mm. gave 0.95 g. of material with b.p. 97–100° and 3.6 g. of colorless oil with b.p. 120–140°; the n.m.r. spectrum of the second fraction indicated a mixture of about 65% of **8b** and 35% of **10b**.

1,2,3-Trimethyl-4-phenylpyrazolium Iodide.—A solution of 3.4 g. of mixed 1,3- and 1,5-dimethyl-4-phenylpyrazole isomers from the enol ether condensation and 5.7 g. of methyl iodide in 1.5 ml. of methanol was heated in a Carius tube at 100° for 48 hr. The tube contents were dissolved in hot water and the solution was filtered to remove a small amount of amorphous solid. On cooling, an oil separated which crystallized on standing. Recrystallization from ethanol–water gave 9 g. of pale yellow needles, m.p. 149°.

Anal. Calcd. for $C_{12}H_{15}IN_2$: C, 45.87; H, 4.81; I, 40.40; N, 8.92. Found: 45.48; H, 4.90; I, 39.66; N, 8.83.

Thermal decomposition of the salt and distillation of the pyrazoles gave an isomer mixture of essentially the same composition as obtained in the condensation and methylation reactions.

The Protonation of Benzoylbenzoic Acids[1,2]

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The behavior of *o*-benzoylbenzoic acid (I) as a simple base in strong sulfuric acid has been examined spectrophotometrically. I is 50% converted to the conjugate acid in about 80% sulfuric acid. The nature of the spectral changes resulting on protonation and the sensitivity of the basicity to substitution both suggest that protonation occurs at the ketonic oxygen. The ionization ratios do not show exact 1:1 correspondence with the acidity function; slopes of log (BH^+/B) *vs.* H_0 are about 0.8.

There has been much recent interest in the protonation of weak bases in fairly concentrated mineral acids. Though the original development of the acidity scale by Hammett suggested that many different classes of compounds would respond similarly to the acid concentration of the medium, more recent investigations have shown that this is not invariably the case. A recent review by Arnett[4] summarizes much of the relevant information. Taft[5a] showed that the protonation equilibria of tertiary amines and primary amines are not parallel in 60–80% sulfuric acid. Recently, Arnett and Mach[5b] established an acidity scale using only tertiary aromatic amines. This scale (designated H_0''' by Arnett and Mach) differs from the original H_0 scale of Hammett and clearly points out that differences in solvation and of activity-coefficient behavior severely limit the general applicability of the H_0 scale. In re-evaluating the H_0 scale, Jorgenson and Hartter[6] used a set of primary amines (anilines). The fact that the acidity scale defined in this way showed some deviations above 60% sulfuric acid from the original scale of Hammett[7] implied that the protonation equilibria of primary amines and of oxygen bases are not invariably parallel.

As the original set of indicators used by Hammett included some ketones and tertiary amines, we also examined the acid–base behavior of benzalacetophenone[8] in more detail than had been done previously. It was found that extreme caution must be used in evaluating the data for chalcone, since the spectral changes with increasing sulfuric acid concentration included not only the formation of the conjugate acid, but also a very pronounced bathochromic shift and a further increase in molar absorbancy. When appropriate corrections were made, the behavior of chalcone as an acid–base indicator was satisfactory.

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[2] For previous paper, see D. S. Noyce, F. B. Miles, and D. R. Hartter, *J. Am. Chem. Soc.*, **86**, 3583 (1964).

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The basicity of other ketones[9–11] measured on the H_0 scale indicated that they do not invariably give ionization ratios showing a 1:1 correlation with the acidity function.

More recently it has been shown that alcohols[12] also vary considerably in the slopes of the log BH^+/B *vs.* H_0 plots.

More striking deviations from the H_0 scale in protonation equilibria are shown by alkenes,[13] by derivatives of phloroglucinol,[14] by azulenes,[15] and by heterocyclic compounds.[16] Deno[13a] has defined a separate acidity function for alkenes as has Hinman for indoles.

Recently the behavior of amides as weak bases has been subjected to careful scrutiny,[17] and it has been suggested[11] that the substantial deviations from "ideal" behavior are the result of specific solvation requirements. A separate acidity scale has been suggested for amides.[18]

In conjunction with other studies,[19] we have had occasion to examine the protonation equilibria of a variety of substituted *o*-benzoylbenzoic acids, and it is the purpose of this report to discuss these results.

Experimental[20]

Preparation of Materials.—*o*-Benzoylbenzoic acid (Eastman Kodak) was recrystallized from carbon tetrachloride and sublimed at 70° (0.05 mm.), m.p. 127.0–128.9° (lit.[21] m.p. 127°).

2-Methyl-4-methoxybenzophenone, b.p. 164–166° (1.5 mm.) [lit.[22] b.p. 219–221° (23 mg.)], was prepared by the Friedel–Crafts reaction of benzoyl chloride and *m*-cresyl methyl ether.

2-Benzoyl-5-methoxybenzoic acid, m.p. 149.6–151.2° (lit.[23] m.p. 155–156°), was prepared by the potassium permanganate oxidation of 2-methyl-4-methoxybenzophenone.

2-Benzoyl-4-methoxybenzoic acid, m.p. 173.4–174.0° (lit.[23] m.p. 172–174°), was prepared by the permanganate oxidation of 1-phenyl-3,4-dihydro-7-methoxynaphthalene[24] prepared from 7-methoxy-1-tetralone.[25]

2-(4-Methoxybenzoyl)benzoic acid, m.p. 144.4–146.4° (lit.[26] m.p. 144–145°), was prepared by the Friedel–Crafts reaction of phthalic anhydride and anisole.

4-Nitro- and 5-nitro-2-benzoylbenzoic acids were prepared by the Friedel–Crafts reaction of 4-nitrophthalic anhydride and benzene. Crystallization from benzene afforded the higher melting isomer, 3-benzoyl-5-nitrobenzoic acid, m.p. 213.0–214.2° (lit. m.p. 212°,[27,28,29] 214–215°[30]). From the mother liquors by crystallization from carbon tetrachloride there was obtained 2-benzoyl-4-nitrobenzoic acid, m.p. 161.4–163.1° (lit. m.p. 164–165°,[31,27] 162°[28]).

2-(3-Nitrobenzoyl)benzoic acid, m.p. 182.2–182.6° (lit. m.p. 186–187°,[31] 186.2–187.5°,[32] 189.0–189.5°[33]), was prepared by the direct nitration of *o*-benzoylbenzoic acid.

2-(4-Methylbenzoyl)benzoic acid was prepared by the Friedel–Crafts reaction of toluene and phthalic anhydride.[34]

4-Methyl- and 5-methyl-2-benzoylbenzoic acids were prepared by the Friedel–Crafts reaction of 4-methylphthalic anhydride and benzene. The isomers were separated by fractional crystallization from a mixture of benzene and hexane. The pure 4-methyl-2-benzoylbenzoic acid melts at 149.4–150.1° (lit.[35] m.p. 149°) and the pure 5-methyl-2-benzoylbenzoic acid melts at 139.2–139.8° (lit.[35] m.p. 136°).

2-(3-Methylbenzoyl)benzoic acid, m.p. 159.2–159.6° (lit.[36] m.p. 162°), was prepared by the reaction of phthalic anhydride and *m*-methylphenylmagnesium bromide.

2-(3-Methoxybenzoyl)benzoic acid, m.p. 154.5–155.4°, was prepared by the reaction of phthalic anhydride and *m*-methoxyphenylmagnesium bromide.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.73. Found: C, 70.52; H, 4.67.

2-(4-Bromobenzoyl)benzoic acid, m.p. 168.8–170.2° (lit.[37,38] m.p. 173°), was prepared by Friedel–Crafts reaction of bromobenzene and phthalic anhydride.

Basicity Measurements.—*o*-Benzoylbenzoic acid shows the development of a new peak in the ultraviolet spectrum, λ_{max} 3000 Å., in 80–90% sulfuric acid. As the sulfuric acid concentration is further increased, this peak is superceded by a new peak, λ_{max} 4050 Å., in 96–98% sulfuric acid. Similar spectral changes are observed with substituted benzoylbenzoic acids.

Spectra were determined using a Cary 14 spectrometer. Generally, after preliminary screening to determine the approximate percentage sulfuric acid in which the first spectral changes occurred, a group of about 8–12 spectra were determined in sulfuric acid solutions closely spaced in percentage. Two problems become apparent in considering the raw data. The behavior of *o*-benzoylbenzoic acid does not follow the ideal for a Hammett indicator; the intensity of the new band at 3000 Å. does not increase so rapidly as would be predicted by a 1:1 correspondence of log I (the ionization ratio, BH^+/B) to H_0. Secondly the spectral change associated with the subsequent indicator reaction (formation of the lactol carbonium ion[39]) begins before the conversion of *o*-benzoylbenzoic acid to its conjugate acid is complete. These two difficulties preclude a straightforward analytical solution of the problem. The Hammett least-squares treatment is not appropriate as it presumes that ionization is directly related to h_0 and not to some fractional power of h_0. A Geissman plot is fairly shallow and thus diffuse. The data were therefore evaluated by a combination of techniques: visual examination of graphs of log I *vs.* H_0; determination of the extinction coefficient for the protonated form of *o*-benzoylbenzoic acid by considering the observed spectrum in 91% sulfuric acid, and correcting for the small fraction of material converted to the lactol carbonium ion[39]; and final calculations using the procedure suggested by Homer and Moodie.[16a] These procedures give good values for the acidities at which the benzoylbenzoic acids are converted to the extent of 50% to the conjugate acids. They also give clear indication of the slope of log I *vs.* H_0. The uncertainties in the latter are somewhat larger than desirable; nevertheless they are acceptable.

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Results and Discussion

The results of the measurement of the protonation equilibria for 12 substituted benzoylbenzoic acids are summarized in Table I.

TABLE I

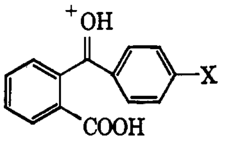
PROTONATION EQUILIBRIA FOR SUBSTITUTED BENZOYLBENZOIC ACIDS

Substituent	λ_{max} (BH$^+$), mμ	Slope log I vs. H_0	H_0 at log I = 0[a]
H	3100	0.67	−7.35
4′-Methyl	3250	0.85	−6.55
4′-Methoxy	3550	0.77	−5.81
4′-Bromo	3400	0.76	−7.63
3′-Methyl	3050	0.90	−6.76
3′-Methoxy	3050	0.95	−7.09
3′-Nitro[b]	...	...	...
5-Nitro	3050	0.73	−8.26
5-Methyl	3000	0.93	−6.48
5-Methoxy	3750	0.87	−6.77
4-Nitro	3100	0.86	−8.35
4-Methyl	3000	0.71	−7.08
4-Methoxy	3050	1.0	−6.8 ± 0.1

[a] This is thus the acidity at which 50% of the substituted benzoylbenzoic acid is converted to the conjugate acid. [b] Medium shifts precluded a determination of the constants for this compound.

Two particular facets of these data need further amplification: one is the conclusion to be drawn regarding the dominant structure for the protonated species, and the second is the effect of substituents on the extent of protonation at a given acidity.

Structural Arguments.—As indicated in Table I, introduction of substituents into the *para* position of the benzoyl ring (4′ substituents) exerts a profound influence on the basicity of the benzoylbenzoic acids. Particularly notable is the influence of a *p*-methoxyl group (compound III). The enhanced basicity strongly bespeaks of protonation on the ketonic carbonyl oxygen (*cf.* structure A).



A

IIIA, X = OMe

Such a conclusion is in accord also with the remainder of the data in Table I. It is to be noted that electron-donating substituents in the 5-position are generally more effective than similar substituents in the 4-position.

On *a priori* grounds as well, such a conclusion is warranted by the consideration of the basicity of aromatic ketones compared with aromatic acids.

The protonation equilibria of a variety of aromatic carboxylic acids have been reported. It was early observed by Hantzsch[40] that aromatic acids are protonated in sulfuric acid; in the early classic studies of Hammett and Deyrup the basicity of benzoic acid was determined.[41] More recently Stewart and Yates[42] have examined an extensive set of aromatic acids. For benzoic acid itself the acidity at which one-half the benzoic acid is protonated is 81.5% H_2SO_4, corresponding to an H_0 of −7.58.[43]

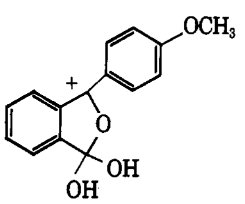
Similarly, extensive studies have been made of aromatic ketones.[9,10,11,44] For benzophenone the apparent pK_{BH^+} was found to be −6.39.[11] Thus, aromatic ketones are generally more basic than aromatic acids. Consideration of substituent constants predicts that a carboxyl function either *meta* or *para* to the site of protonation will decrease the basicity by about a factor of 10. Similarly the electron-withdrawing nature of a benzoyl group,[45] considered as a substituent on benzoic acid, would be expected to reduce the basicity of the carboxyl group as a site of protonation.

Though it is hazardous to extend $\rho-\sigma$ correlations to *ortho*-substituted compounds, nevertheless the prediction made on this basis is most satisfactorily in accord with the ketonic group as the site of protonation of *o*-benzoylbenzoic acids.[46]

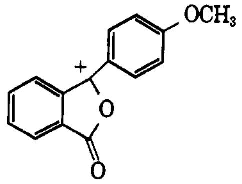
Spectral Shifts.—The spectra of the conjugate acids of the benzoylbenzoic acids also support the conclusion that the site of protonation is the ketone function.

Introduction of a 5-methoxy or of a 4′-methoxy substituent results in a pronounced shift to longer wave lengths for the protonated form. This is of course in accord with the effect of this substituent on the spectra of many other families of compounds, *e.g.*, the shift observed with benzophenones.[11]

Thus structure IIIA seems most adequate to describe the protonated benzoylbenzoic acids. An alternative, IIIB, appears unsatisfactory, particularly if one takes cognizance of the spectrum of *o*-benzoylbenzoic acid in 100% sulfuric acid. The long-wave-length absorption maximum for III in 100% sulfuric acid appears at 4400 Å., in accord with structure IIIC. It would be expected that IIIB would be very similar to IIIC in spectrum.



IIIB



IIIC

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Effect of Structure on Basicity.—When the data of Table I are considered for use in making ρ–σ correlations, the general nature of the correlation pattern is evident, and indeed has been anticipated in the preceding discussion. However, as the protonation equilibria do not follow H_0 with unit slope (*i.e.*, the slope of a plot of log $[BH^+/B]$ *vs.* H_0 is not unity), there is some ambiguity in the value to be gained from a complete numerical treatment of the basicities of the substituted benzoylbenzoic acids. In addition to the data which we have presented here Vinnik[47] recently reported data on two other substituted benzoylbenzoic acids. His reported data for *o*-(3,4-dimethylbenzoyl)benzoic acid and *o*-(2-chlorobenzoyl)benzoic acid are in accord with ours, with the exception of the value for the parent compound.

Hammett Base Character of the Protonated Benzoylbenzoic Acids.—The summarized slopes of log $[BH^+/B]$ *vs.* H_0 show that the benzoylbenzoic acids are not behaving as ideal Hammett indicators. Such deviation from ideality is also shown by substituted benzophenones; the slope for benzophenone is *ca.* 0.86, and that for *p,p'*-dimethoxybenzophenone is 0.87.

Such deviations have been ascribed to differences in the solvation requirements of ions of different structure. The difference between primary and tertiary amines has been ascribed to changes in solvation requirements,[5] and similar arguments have been advanced as an explanation of the behavior of amides as weak bases.[16a] It would appear reasonable that a like explanation is valid also in the present instance. Unfortunately the spectral changes accompanying the protonation of benzoylbenzoic acid are complex. There is a considerable bathochromic medium shift (apparently common for oxygen bases; *cf.* benzalacetophenone[8] and benzoic acid[41]). This factor, coupled with the subsequent structural changes in more concentrated sulfuric acid, precludes the determination of extremely precise data for this family of compounds. Hence the general pattern is clear, but the precision of the data is only moderate. Benzoylbenzoic acids are weak bases, protonate at the ketonic carbonyl group, and generally do not behave as primary aniline Hammett bases; the effect of substituents on basicity is in accord with this expectation.

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The Effect of Substituents upon the Formation of the Lactol Carbonium Ion of Benzoylbenzoic Acid[1-4]

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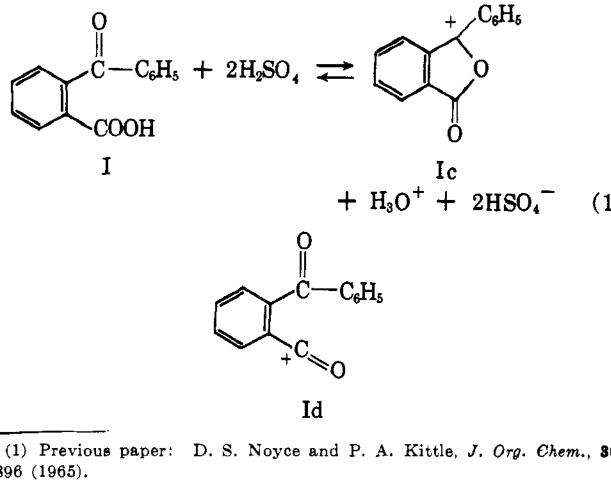
It is shown by consideration of structural effects and spectral characteristics that the lactol carbonium ion (Ic) is the best representation of *o*-benzoylbenzoic acid in concentrated sulfuric acid. Correlations of the effect of structure on the ease of formation of Ic are best with σ^+ values, ρ being 1.83.

In conjunction with other studies[2,5] we have had occasion to examine the behavior of a group of substituted *o*-benzoylbenzoic acids in 90–100% sulfuric acid. Newman, Kuivila, and Garrett[6] have shown that *o*-benzoylbenzoic acid (I) undergoes "complex ionization" (eq. 1) in 100% sulfuric acid in support of the earlier suggestion of Newman[7] that the dominant species in such solutions is Ic. Newman considered it less likely that the major species in 100% sulfuric acid is the open-chain acylium ion Id, since a mixture of normal and pseudo-ester is obtained on pouring a solution of I in 100% sulfuric acid into methanol. Long and Paul[8] have pointed out that the cryoscopic results[6] do not serve to distinguish between Ic and Id. Vinnik, Ryabova, and Chirkov[9] have obtained data showing that the product of complex ionization is formed to the extent of 50% in 96% sulfuric acid, though they prefer to describe it in terms of structure Id.



I

Ic

$+ H_3O^+ + 2HSO_4^-$ (1)

Id

It is the purpose of the present report to describe the results of measurements relating to the effect of substituents on the ease of formation of the lactol carbonium ion Ic; it will also be clear that Ic is the better structure for the dominant species in solution in 100% sulfuric acid.

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[4] National Science Foundation Cooperative Fellow, 1961–1962; National Institutes of Health Predoctoral Fellow, 1962–1963.

[5] D. S. Noyce and P. A. Kittle, manuscript in preparation.

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[9] M. I. Vinnik, R. S. Ryabova, and N. M. Chirkov, *Zh. Fiz. Khim.*, **33**, 1992 (1959); *Russ. J. Phys. Chem.*, (Eng. Transl.), **33**, 253 (1959).