removed by filtration, the acetone was recovered and 3.9 g. of ethyl picolinoylacetate was added. After 48 hr., the solution was concentrated to 30 ml., cooled, and filtered. A crystalline solid was obtained which was recrystallized from dilute ethanol providing 0.4 g. (8% based on ethyl picolinoylacetate) of colorless needles, m.p. 222.5–223.0°.

Anal. Calcd. for $C_{14}H_{10}N_4O$: C, 67.18; H, 4.03. Found: C, 67.25; H, 4.37.

2-Methyl-2,4,6-tris(2'-pyridyl)-1,2-dihydro-s-triazine (VI). A solution of 3.1 ml. of methyl iodide in 10 ml. of ether was added dropwise to a suspension of 1.1 g. of lithium metal in 10 ml. of anhydrous ether. The resulting solution was siphoned through a tube containing a glasswool plug into 20 g. of 2-cyanopyridine. Cooling was necessary in order to control the rapid exothermic reaction which ensued. Excess chopped ice was added and the insoluble material was removed by filtration to give 0.4 g. of a colorless solid, m.p. 243–244°, undepressed by admixture with an authentic sample of tris(2'-pyridyl)-s-triazine trihydrate (I).[8]

The aqueous portion of the filtrate was extracted with 60 ml. of ether. The combined ethereal solutions were dried over potassium sulfate and concentrated to 30 ml. Upon standing, a crystalline, yellow solid separated which was recrystallized from petroleum ether (b.p. 90–100°) yielding 3.7 g. of pale yellow solid, m.p. 163.0–163.5°.

Anal. Calcd. for $C_{19}H_{16}N_6$: C, 69.49; H, 4.91. Found: C, 69.97; H, 5.10.

2,4,6-Tris(2'-pyridyl)pyrimidine (VII). When 1.0 g. of VI was heated to 300°, ammonia was rapidly evolved. The resulting residue was recrystallized from methanol to give 0.71 g. (76%) of colorless needles, m.p. 255.5–256.5°.

Anal. Calcd. for $C_{19}H_{13}N_5$: C, 73.30; H, 4.21. Found: C, 73.75; H, 4.31.

3,6-Bis(2'-pyridyl)-1,2,4,5-tetrazine (VIII) was prepared by a modification of the procedure subsequently reported by Dallacker.[7] A solution of 10.4 g. (0.1 mole) of 2-cyanopyridine and 13.4 g. (0.4 mole) of 95% hydrazine in 50 ml. of absolute ethanol was refluxed gently for 6 hr. The resulting orange precipitate was removed and recrystallized from ethanol providing 9.1 g. (76%) of the dihydro base, large yellow needles, m.p. 193–194° (lit.,[7] m.p. 194.2°).

The dihydro base obtained above was dissolved in 50 ml. of glacial acetic acid, and 8.0 ml. of concentrated nitric acid was added dropwise with cooling. Excess chopped ice was added and the mixture was made distinctly alkaline by the addition of sodium bicarbonate. The crystalline precipitate was separated and washed with ethanol to give 5.5 g. (64%) of VIII, a deep red solid, m.p. 222° dec. (lit.,[7] m.p. 224.5°).

3,6-Bis(2'-pyridyl)pyridazine (IXa). Acetylene was slowly bubbled through refluxing dimethylformamide containing 1.0 g. of finely divided VIII. The disappearance of the red color indicated the completion of the reaction. The solvent was recovered by distillation and the solid residue was recrystallized from absolute ethanol producing 0.79 g. (84%) of colorless needles, m.p. 179–180°.

Anal. Calcd. for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30. Found: C, 71.80; H, 4.35.

3,6-Bis(2'-pyridyl)-4-phenylpyridazine (IXb). One gram of VIII was added to a solution of 0.50 g. of phenylacetylene in 25 ml. of toluene. The resulting mixture was refluxed overnight. After this time the red color of the tetrazine had disappeared. The solid residue which remained after recovery of the solvent was recrystallized from ethanol to give 0.90 g. (68%) of colorless needles, m.p. 177.5–178.5°.

Anal. Calcd. for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55. Found: C, 77.24; H, 4.66.

3,6 - Bis(2' - pyridyl) - 4 - cyano - 1,4 - dihydropyridazine (X). A procedure identical with that just outlined above was used except that acrylonitrile was used in place of phenylacetylene. From 1.6 g. of VIII and 1.1 g. of acrylonitrile was obtained 1.2 g. (68%) of yellow needles, m.p. 137–138°.

Anal. Calcd. for $C_{15}H_{11}N_5$: C, 68.95; H, 4.24. Found: C, 68.81; H, 4.29.

3,6 - Bis(2' - pyridyl) - 4 - cyanopyridazine (IXc). A solution of 0.18 g. of potassium dichromate in 1.5 ml. of water was added to 0.42 g. of X in 7.5 ml. of glacial acetic acid. The mixture was refluxed gently for 1 hr. and then was neutralized with concentrated aqueous ammonia. The resulting precipitate was recrystallized from ethanol, providing 0.21 g. (54%) of pale yellow needles, m.p. 206–207°.

Anal. Calcd. for $C_{15}H_9N_5$: C, 69.49; H, 3.50. Found: C, 69.80; H, 3.44.

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On the Generality of the Hammett Equation

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Hine has shown that a check of the general applicability of the Hammett equation is the constancy of the σ-difference ratio

$$\frac{\sigma_{p\text{-}x_1} - \sigma_{p\text{-}x_2}}{\sigma_{m\text{-}x_1} - \sigma_{m\text{-}x_2}}$$

where the σ's are substituent constants for x_1 and x_2 groups in the *meta* or *para* position.[2] Using the σ-constants for $—NO_2$, $—OCH_3$, —F, and $—CH_3$ groups as examples it was concluded that with the presently known σ-values "the unmodified Hammet equation could not possibly fit the equilibrium constants of *m*- and *p*-substituted benzene derivatives in general." This conclusion applies to direct substitution on the aromatic ring. It has generally been assumed that the Hammett equation may be applicable to many, if not all, equilibria involving only side-chain reactions although practically all of the equilibria which are known[3] to follow the Hammett equation are simply ionization equilibria. Hine's criterion provides a means to test the generality of the Hammett equation as applied to side chains.

In order to apply Hine's criterion to equilibria involving only side chain reactions it is necessary in computing the σ-difference ratio to use only σ-constants for substituents having the same atom attached to the aromatic ring. As the σ-difference ratio represents the slope of the line joining two points in a plot of σ_p vs. σ_m, plots were made for all of the values obtained from the dissociation constants of benzoic acids where data were available for at least two points.[4,5] Fig. 1 shows the results.

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[2] J. Hine, *J. Am. Chem. Soc.*, **81**, 1126 (1959).

[3] R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, 81, 5343 (1959).

[4] Sigma constants from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

Nine points are available for carbon substituents and, within the estimated uncertainty of the σ-values, these fit on a straight line, demonstrating the constancy of the σ-difference ratio. For sulfur substituents six points are available, and again, within the estimated uncertainty of the σ-values a straight line is obtained. For nitrogen and iodine substituents there are only three and two points respectively. The line for iodine accordingly would have only trivial significance except that it has the same slope as the better established lines. Oxygen substituents conspicuously fail to give a straight line. The plots, taken with Hine's criterion, indicate that side chain equilibria of the type $RArCH_3 \rightleftharpoons RArCF_3$, $RArSCH_3 \rightleftharpoons RArSO_2CH_3$, or $RArNH_2 \rightleftharpoons RArNO_2$ (*i.e.*, equilibria involving a change between any substituents falling on one of the straight lines in Fig. 1.) might possibly be correlated using presently known σ-values and a single ρ for both *m*- and *p*-derivatives. On the basis of the plots a correlation is not expected for $RArOH \rightleftharpoons RArOCH_3$. These equations are, of course, only half reactions and do not include the reaction of the reagent bringing about the transformation.

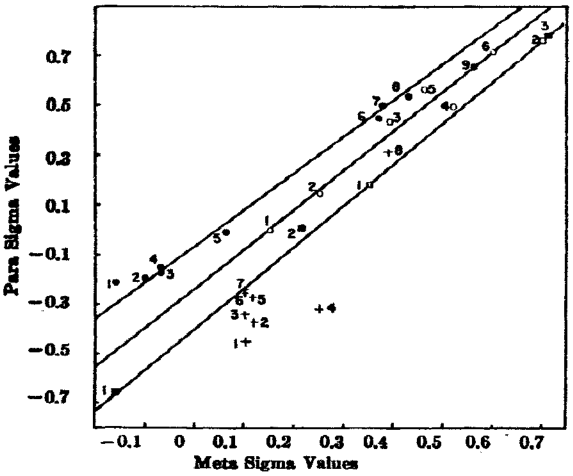

Fig. 1. *para* Sigma values *vs.* *meta* sigma values for dipolar groups. Closed circles are carbon family: 1 = $—CH_2Si(CH_3)_3$, 2 = $—C(CH_3)_3$, 3 = $—CH_3$, 4 = $—C_2H_5$, 5 = $—C_6H_5$, 6 = $—CO_2C_2H_5$, 7 = $—COCH_3$, 8 = $—CF_3$, 9 = —CN. Open circles are sulfur family: 1 = $—SCH_3$, 2 = —SH, 3 = $—SCOCH_3$, 4 = $—SOCH_3$, 5 = $—SO_2NH_2$, 6 = $—SO_2CH_3$. Closed squares are nitrogen family: 1 = $—NH_2$, 2 = $—NHCOCH_3$, 3 = $—NO_2$. Open squares are iodine family: 1 = —I, 2 = IO_2. Plus signs are oxygen family: 1 = $—OCH(CH_3)_2$, 2 = —OH, 3 = $—OC(CH_3)_3$, 4 = $—OC_6H_5$, 5 = $—OCH_3$, 6 = $—O(CH_2)_2CH_3$, 7 = $—OC_2H_5$, 8 = $—OCOCH_3$. The lines were constructed by treating each point as the center of an ellipse whose axes are equal to twice the limits of uncertainly given in ref. 4. Each line was then visually constructed so as to pass through all ellipses. In the case of the carbon family the line was virtually determined by the points 2, 3, and 7 because of the small estimated limits of uncertainty of these points.

Charged groups are not shown in Fig. 1. These groups do not fit in with the dipolar groups but give a linear relationship of their own (Fig. 2). The σ-values of the $—O^-$ group cannot be evaluated from benzoic acid ionization data but Jaffé's σ-values for this group fit excellently on the plot and may be taken as support for his assignments.[6] The σ-values for the $—N_2^+$ group do not fit, apparently due to a strong inductively relayed resonance effect of the $p\text{-}N_2^+$ group.[7] The σ-difference ratio for charged groups is only 0.9 as compared to 1.5 for dipolar substituents. This indicates that it may be inappropriate to apply conclusions based on the σ-values of charged groups to systems involving dipolar groups. Taft's assignment of equal inductive effects for a substituent in the *meta* or *para* position is based in part on the σ-values of the charged trimethylamino group.[8] The τ-values calculated by Hine utilize σ-values of both a neutral and a charged substituent and hence these τ-values may be applicable only to ionization equilibria.[2]

Although the plots shown in Figs. 1 and 2 were constructed in order to test the generality of the Hammett equation, it is reasonably obvious that the linear relationships may be used for predictive purposes. The dissociation constant of a *para* substituted benzoic acid may be predicted from the value for the *meta*-derivative and *vice-versa*, provided that the *meta*- and *para*-constants are known for at least one other member of the same side chain type (or preferably that the line for the family has been established). Or, an equation of the form $\sigma_p = m\sigma_m + b$ may be written for a given family of substituents where $m \approx 1.5$ for dipolar substituents and for carbon b = −0.06, for sulfur b = −0.24, and for nitrogen or iodine b = −0.40. This equation, combined with Taft's equations relating to inductive and resonance effects,[9] allows the σ-values (with reference to benzoic acid) to be calculated from the inductive con-

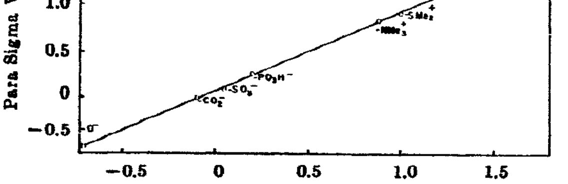

Fig. 2. Para sigma values *vs.* meta sigma values for charged groups.

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(5) Strict application of Hine's criterion requires that the sigma values be obtained for an equilibrium in a fixed solvent and at constant temperature. The σ-values used here include not only those where water is a solvent but also some where aqueous ethanol is the solvent.

(6) H. H. Jaffé, *Chem. Revs.*, 53, 191 (1953).

(7) E. S. Lewis and M. D. Johnson, *J. Am. Chem. Soc.*, 81, 2070 (1959).

(8) Ref. 3, footnote 9.

(9) Ref. 3, Equations 1–4.

stants derived from aliphatic compounds through the relationship

$$\sigma_m = \frac{1 - \alpha}{1 - \alpha m}\,\sigma_{\rm I} + \frac{\alpha b}{1 - \alpha m}$$

Using the α-value of Roberts and Jaffé[10] this equation is simply $\sigma_m = 1.18\,\sigma_{\rm I} + b/3$.

Finally, it should be stated that although σ-values were used, the identical plots would be obtained if pK_a- values had been plotted for the benzoic acid system. Plots of pK_a- values for phenols and anilinium ions show much greater deviations from linearity than found in the benzoic acid family. Resonance interactions seem to offer a possible explanation for some of these deviations. This suggests that of the dipolar groups shown in Fig. 1, only the oxygen substituents are strongly conjugated with the carboxyl group.

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ADDED IN PROOF: Nathan L. Bauld presented at the 139th A. C. S. Meeting (March 1961) a relationship similar to that given in Fig. 1 accompanied with a theoretical approach differing from that given here.

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[10] J. L. Roberts and H. H. Jaffé, *J. Am. Chem. Soc.*, **81**, 1635 (1959).

Norbornadiene–Silver Nitrate Complexes[1,2]

JAMES G. TRAYNHAM

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Two descriptions of norbornadiene–silver nitrate complexes have been published.[3,4] On the basis of a silver analysis only, the complex precipitated from aqueous solution was first inferred to be $C_7H_8 \cdot AgNO_3$ (1:1 complex).[3] The later report described a product, recrystallized from ethanol, which gave carbon, hydrogen and silver analyses in agreement with the formula $C_7H_8 \cdot 2AgNO_3$ (1:2 complex).

Because of the implications of the composition of the complex for conjugative properties in the diene,[3] this system has now been reexamined and additional data have been collected. The white solid which is initially precipitated from 1*M* silver nitrate solution by the addition of norbornadiene gives analyses which are not in agreement with either the 1:1 or the 1:2 formula. Instead, the found values for carbon, hydrogen and silver lie in between those calculated for the 1:1 complex and the 1:2 complex. Different preparations have different compositions, and sometimes the silver analysis is close to that required by the 1:1 formula.[3] Contamination of the 1:2 complex by neither water nor silver nitrate would lead to both low silver and high carbon-hydrogen analyses. The most reasonable inference about this initially-precipitated material is that it is a mixture of 1:1 and 1:2 complexes whose exact proportions vary from preparation to preparation. On this assumption one may calculate the composition of the material. Two analyses, for example, indicate compositions of 51% and 32% of 1:1 complex, respectively.

When the initially-precipitated material is either recrystallized from ethanol[4] or is stirred well with water and then rinsed on a suction filter with cold alcohol and ether, the resulting white solid gives analyses for a 1:2 complex. Unlike the initial precipitate, which chars over a rather wide temperature range, the recrystallized material melts sharply. The 1:1 complex apparently is the more soluble and is readily removed by thorough washing with water or by recrystallization from ethanol.[5]

Attempts to prepare the pure 1:1 complex have been unsuccessful, but they have nonetheless provided evidence for the existence of such species in the mixture. When pure 1:2 complex was recrystallized from ethanol containing 10% of norbornadiene, the white needles gave analyses corresponding to a mixture of 27% of the 1:2 complex and 73% of the 1:1 complex. This mixture readily lost norbornadiene during extended suction filtration and subsequent standing in air; the composition returned to that of the 1:2 complex. It seems highly unlikely that the forming crystals would selectively occlude the minor component of the solvent mixture to the complete exclusion of the major component. It is possible however that the geometry of the norbornadiene molecule permits it to fit in holes in the crystal structure, without otherwise being chemically bound to the silver ions, and that ethanol molecules are unsuited for this. In order to examine this possibility, the pure 1:2 complex was recrystallized from a mixture of ethanol and norbornane. Achievement of exactly identical steric requirements for a diene and its saturated analog is not possible, of course, but norbornadiene and norbornane probably duplicate one another about as closely as possible. Were it merely a matter of shape and size, the nearly-identical norbornane molecules probably would substitute for the norbornadiene ones incorporated into the crystals in

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[1] This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] A substantial part of this investigation was carried out at Eidg. Technische Hochschule, Zurich, Switzerland, while the author was on sabbatical leave from Louisiana State University during 1959–1960.

[3] J. G. Traynham and J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959).

[4] E. W. Able, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, **1959**, 3178.

[5] The formation of cyclooctatetraene–silver nitrate complexes of different compositions by different methods of preparation has been described; A. C. Cope and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2515 (1950).