As a further check on the importance of steric effects in the 2-phenyl ring, the reaction rate of 2-mesityl-4,5-diphenylimidazolyl (IIx) was measured and compared with that for 2-*o*-tolyl-4,5-diphenylimidazolyl (IIv). If steric considerations were important, the former compound should react faster, while, if the electronic effect of the methyl groups were the primary determinant of the rate, the latter compound would be the more reactive. The rate constant for the mesityl compound is $2.35 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, some 17 times greater than that for the ortho methyl substituted radical. This difference is probably a lower limit, since the steric effect of the ortho methyl groups in the mesityl compound is negated somewhat by the electronic effect of that radical's para methyl substituent.

It is interesting to note that, whereas ortho disubstitution in the 2-phenyl ring tends to increase the imidazolyl radical's reactivity toward electron abstraction, it decreases its dimerization rate.[16] These two phenomena have the same basic cause. The formation of the thermally stable 1,2′ isomer is severely hindered in a ortho disubstituted radical with the 2-phenyl ring preferring a conformation nearly perpendicular to the imidazole ring plane. In this conformation, the ortho substituents on the 2-phenyl ring lie above and below the carbon at position two, effectively shielding it from bond formation with a second radical's imidazole nitrogen. Thus, the same steric factor which tends to make imidazole radicals more reactive toward electron abstraction also makes them more resistant to dimerization.

Experimental Section

Materials.—Tris(2-methyl-4-diethylaminophenyl)methane was kindly donated by E. Urban, Organic Chemicals Department, Du Pont. Samples of triphenyl-, 2-*o*-chlorophenyl-4,5-diphenyl-, 2-*o*-bromophenyl-4,5-diphenyl-, and 2-mesityl-4,5-diphenylimidazolyl dimer were prepared by Cescon, Coraor, *et al.*[5] The properties of new hexaarylbiimidazoles used in this study and their triarylimidazole precursors are listed in Tables III and IV. They were prepared by methods described by Cescon, Coraor, *et al.*[5] The wide melting ranges reported for many of the dimers are due to their thermal instability and, perhaps, in part to their tendency to strongly retain solvent of crystallization.[5] The latter is most probably the cause of the occasional lack of exact agreement between calculated and found microanalytical values.

Apparatus.—The flash photolysis apparatus was of conventional design.[7,17] Light from the analysis lamp was filtered through a Corning 3-69 filter before entering the sample cell and through a Corning 3-72 filter before entering the monochrometer. The photolyzing radiation was restricted to the ultraviolet with a Corning 7-54 filter. The kinetic studies were performed at 25 ± 2°.

Registry No.—6, 4482-70-6.

Acknowledgment.—The author is grateful to Drs. Richard G. Bennett and Alexander MacLachlan for permission to use the flash photolysis equipment at the Radiation Physics Laboratory of the Du Pont Company.

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[16] Unpublished data, R. L. Cohen.

[17] G. Porter, *Proc. Roy. Soc., Ser. A*, **200**, 284 (1950).

Substituent Effects on the Basicity of Pyridine. Elucidation of the Electronic Character of β-Substituted Vinyl Groups

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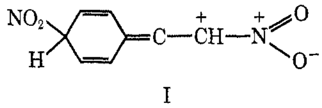
Pyridines substituted in the 3 and 4 positions by groups $-CH{=}CHX$, where $X = NO_2$ (only the 3-substituted compound), CN, CHO, $COCH_3$, $COOC_2H_5$, COC_6H_5, $COC_6H_4NO_2$, have been synthesized and their pK_a values measured. The correlation of pK_a values of substituted pyridines with the Hammett equation is discussed, with particular regard to the above substituents. Also prepared were *m*- and *p*-vinylbenzoic acids, and substituent constants for the vinyl group of 0.08 (σ_m) and -0.08 (σ_p) have been established.

Halogeno substituents are well known for their ability to direct electrophilic attack at the positions ortho and para to their point of attachment to a benzene ring, but reducing the rate of attack below that of benzene itself. This is attributed in simple terms to the opposing influence of the mutually independent inductive and resonance effects. A similar situation arises in the case of the β-nitrovinyl substituent and other substituents made up of attachment of a group of −I or (−I, −M) character to the β position of the vinyl group. Thus Truce and Simms[2] found only 2% of meta nitration in β-styryltrimethylammonium picrate, while Baker and Wilson, Underwood and Kochmann, and Bordwell and Rohde obtained analogous results with β-nitrostyrene,[3] cinnamic acid,[4,5] and β-styrenesulfonyl chloride.[5] The latter workers also demonstrated correspondence between the rate of nitration of such compounds and that of chlorobenzene. These and other workers[6,7] have consequently likened the electronic character of such substituents to that of the halogens, while at the same time remarking on the apparent high energy of the canonical form I involving adjacent positive charges of the Wheland intermediate resonance hybrid for para nitration of β-nitrostyrene.



I

Stewart and Walker[7] have also measured the dissociation constants for the *m*- and *p*-β-nitrovinyl derivatives of benzoic acid and thus shown that the σ_m and σ_p

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[1] Munton and Fison Ltd., Stowmarket, Suffolk, England.

[2] W. E. Truce and J. A. Simms, *J. Org. Chem.*, **22**, 762 (1957).

[3] J. W. Baker and I. S. Wilson, *J. Chem. Soc.*, 842 (1927).

[4] H. W. Underwood and E. L. Kochmann, *J. Amer. Chem. Soc.*, **48**, 254 (1926).

[5] F. G. Bordwell and K. Rohde, *ibid.*, **70**, 1191 (1948).

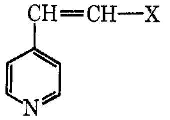
[6] L. N. Ferguson, *J. Chem. Educ.*, **32**, 42 (1955).

[7] R. Stewart and L. G. Walker, *Can. J. Chem.*, **35**, 1561 (1957).

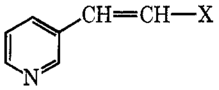
values are closely similar to those for iodine. The implication of this interesting result is that the conjugation of the nitro group with the double bond is far weaker than expected. Thus, despite the fact that the substituent is no longer joined to a nucleus in the transition state of electrophilic substitution, and thus bears a positive charge in conjugation with it, the substituent still acts overall as of (−I, +M) rather than (−I, −M) character.

We were therefore prompted to extend the determination of σ values to other groups of potentially the same electronic character to see if this behavior was general. It was apparent, however, that the range of values encompassed by such groups would be small compared with the overall extent of σ values. It thus seemed necessary to carry out measurements using a reaction site which gave a good correlation with σ, but had a large ρ value. A suitable system appeared to be the pyridinium ion–pyridine equilibrium which in water has a sixfold greater sensitivity than the benzoic acid system to substituent effects.[8]

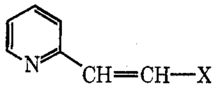
Compounds **2**, **3**, and **4** were generally prepared by base-catalyzed condensation between 2-, 3-, or 4-pyridinecarboxaldehyde and CH_3X; the majority of these compounds had been prepared previously. *p*- (**5a**) and *m*-vinylbenzoic acids (**5b**) were also prepared.



2a–g



3a–g



4f

a, X = NO_2
b, X = CN
c, X = CHO
d, X = $COCH_3$
e, X = $COOC_2H_5$
f, X = COC_6H_5
g, X = $COC_6H_4NO_2$

Experimental Section

Melting points were uncorrected. Infrared spectra were measured on a Perkin-Elmer 257 grating spectrometer. Nmr spectra were taken on a Perkin-Elmer R12 60-MHz spectrometer, using tetramethylsilane as a standard. Peaks were integrated and the proton assignments indicated in all cases corresponded to the areas thus measured. The choice of solvents was dictated by ease of solution and convenience, as no systematic correlation or complex interpretation was intended; the sole purpose of the nmr measurements was for authentication of the compounds. Mass spectra were taken with a Hitachi Perkin-Elmer RMU-6E spectrometer operating with an ionization energy of 70 eV.

Pyridine and 4-vinylpyridine were commercial samples. They were distilled under reduced pressure just before use.

Compounds **2b**,**d–g** and **3a–g** and the Michael addition product from **2f** were obtained by literature methods.[9,10] Yields and melting points were in agreement with previous workers. Nmr spectra of all the compounds were run, generally in CF_3COOH, and in all cases the proton assignments were compatible with the proposed (trans) structures.

4-β-Formylvinylpyridine[11] (**2c**).—4-Pyridinecarboxaldehyde (15.0 g) was dissolved in water (25 ml) containing Amberlite IR-4B (OH) ion-exchange resin (10.0 g). Acetaldehyde (8 ml) in water (20 ml) was added with stirring over 20 min. A yellow precipitate was formed which persisted until the temperature of the solution was raised to 50°. A further addition of acetaldehyde (3 ml) in water (10 ml) was made and the dark brown solution stirred at 40° for 5 hr. The solution was allowed to stand overnight at 25° and then was extracted twice with chloroform (two 100-ml portions). The solvent layer was dried (anhydrous Na_2SO_4) and the solvent removed on a rotary evaporator. The resulting brown liquid was distilled at reduced pressure giving unreacted 4-pyridinecarboxaldehyde (5.5 g). The residue was refluxed for 30 min with *n*-hexane (100 ml) and the hexane layer was decanted. On long standing, it deposited white needles of **2c** (0.07 g, 0.6%), mp 39–41°. *Anal.* Calcd for C_8H_8NO: C, 72.17; H, 5.30; N, 10.52. Found: C, 71.89; H, 5.34; N, 10.51.

The mass spectrum showed m/e (M^+) 133. The ir spectrum showed peaks at 1684 (C=O), 1632, 980 cm^{-1} (trans C=C); nmr (CCl_4) τ 0.49 (d, J = 7 Hz, CHO), 1.53 (m, 2 and 6 H), 2.77 (m, 3 and 5 H and α-vinyl H), 3.35 (two d, J = 17 and 7 Hz, β-vinyl H).

***m*-Vinylbenzoic Acid** (**5b**).—Isophthalaldehydic acid (20 g prepared by the method of Landgrebe and Rynbrandt[12a]) was dissolved in anhydrous ethanol (50 ml) saturated with dry HCl, and the solution was refluxed for 4 hr while HCl was bubbled in. The ethanol was evaporated, water added (20 ml), and the solution extracted with ether. The ethereal solution was dried (anhydrous Na_2SO_4), the ether removed, and the ethyl isophthalaldehydate distilled, bp 122–124° (6 mm) (15.4 g, 71%).

The formyl was converted to the vinyl group by the Wittig reaction. Triphenylphosphonium methyl bromide (40 g) in benzene (100 ml) was refluxed for 4 hr with sodium hydride (9.2 g of 50% in liquid paraffin), and the resulting yellow suspension was refluxed for a further 6 hr with ethyl isophthalaldehydate (10 g). The cold mixture was then poured into water (100 ml) and extracted with benzene. The benzene was removed, leaving an orange solid and a pale green oil. The oil was removed and distilled, bp 82–84° (2 mm) (1.30 g, 12%).

The ethyl *m*-vinylbenzoate (0.2 g) was refluxed for 6 hr with ethanol (0.5 ml), water (3 ml), and NaOH (1 g). The solution was acidified with dilute HCl and the resultant solid filtered off. Recrystallization from water gave white platelets, mp 92–94° (0.15 g, 82%) (lit.[12b] mp 95–96°).

The mass spectrum showed m/e (M^+) 148. The ir spectrum gave bands at 3000 (strong and very broad, OH), 1700 (strong, C=O), and 1610 cm^{-1} (weak, C=C); nmr (CCl_4) τ −3.0 (s, OH), 1.85 and 2.40 (m, 2, 4, 5, and 6 H), 3.12 (q, J_{trans} = 17, J_{cis} = 11 Hz, C_6H_4CH), 4.10 (d, J_{trans} = 17 Hz, $-C_6H_4-CH{=}CH-$). Both the latter doublets showed fine splitting (~1 Hz) due to gem coupling.

***p*-Vinylbenzoic Acid** (**5a**).—The method of preparation was that of Jäger and Waight.[13] The product was recrystallized from water to yield white crystals, mp 144° (lit.[13] 140°). The ir spectrum agreed with that of Jäger and Waight; nmr (CF_3COOH, obscuring acidic proton) τ 1.87 (d, J = 8 Hz, 2 and 6 H), 2.45 (d, J = 8 Hz, 3 and 5 H), 3.15, 4.09, and 4.55 (vinyl H's with coupling characteristics identical with those of the *m*-vinylbenzoic acid spectrum).

pK_a Determinations.—Measurements were carried out at 25° using the spectrophotometric method[14a] for all compounds except 3-β-nitrovinylpyridine where coincident free base and conjugate acid uv spectra necessitated use of the potentiometric method.[7,14b]

Uv spectra were scanned on a Perkin-Elmer Ultracord 316 spectrometer, analytical wavelengths selected, and readings at those wavelengths recorded on a Unicam SP 500 spectrometer (see Table II). Table I shows a specimen determination, 4-β-cyanovinylpyridine.

Results and Discussion

Marvel[9] has reported that the synthesis of **2f** and **4f** led also to the formation of Michael-type addition

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[8] A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 3591 (1964).

[9] C. S. Marvel, L. E. Coleman, and G. P. Scott, *J. Org. Chem.*, **20**, 1785 (1955).

[10] J. Klosa, *Arch. Pharm.* (*Weinheim*), **289**, 177 (1956); Z. S. Ariyan and H. Suschitzky, *J. Chem. Soc.*, 2242 (1961); A. R. Katritzky and A. M. Monro, *ibid.*, 150 (1958); A. R. Katritzky, A. M. Munro, and J. A. T. Beard, *ibid.*, 3721 (1958); P. R. Falkner and D. Harrison, *ibid.*, 2148 (1962); C. S. Marvel and J. K. Stille, *J. Org. Chem.*, **22**, 1451 (1957); M. Strell and E. Kopp, *Chem. Ber.*, **91**, 162 (1958); A. Dornow and F. Boberg, *Justus Liebigs Ann. Chem.*, **578**, 101 (1952); M. Strell and E. Kopp, *Chem. Ber.*, **91**, 2854 (1958).

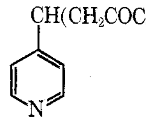
[11] J. G. Carey, British Patent 1,198,221.

[12] (a) J. A. Landgrebe and R. H. Rynbrandt, *J. Org. Chem.*, **31**, 2585 (1966); (b) W. J. Dale, L. Starr, and C. W. Strobel, *ibid.*, **26**, 2225 (1961).

[13] P. Jäger and E. S. Waight, *J. Chem. Soc.*, 1339 (1963).

[14] A. Albert and E. P. Serjeant, "Ionisation Constants of Acids and Bases," Methuen and Co. Ltd., London, 1962: (a) Chapter 4; (b) Chapter 2.

products. Since those by-products do not arise in the preparation of **3f**, it might be conjectured that the true structures were those arising from β attack on **2f** and **4f** by a second carbanion due to mesomeric withdrawal by the pyridine ring. However, nmr studies revealed that the alternative structures **6** and **7**, as suggested by Marvel, were correct.



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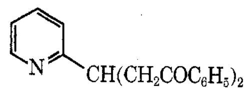

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Both spectra showed a triplet at τ 5.5 (area 1) and a doublet at τ 6.0 (area 4), confirming that addition of the second carbanion from acetophenone takes place on the α carbon atoms of **2f** and **4f**.

The conversion of the pK_a's in Table II to σ values involves use of the appropriate ρ value for the pyridinium–pyridine equilibrium. Fischer and Vaughan[8] have demonstrated with a selected number of substituents (H, 3-CH_3, 3-Cl, 3-Br, 3-$COOCH_3$, 3-CN, and 3-NO_2) that this value is 6.01, and it is not sensibly altered by incorporation of their other substituents values or pK_a's from other workers (with the exception of 4-(−I, −M) groups, which are known to follow σ_I[8,15]).[16] Use of this ρ value leads to the σ values shown in Table III. These indicate that all these substituents are of (−I, +M) type. The M effect arises from the conjugation of the double bond with the aromatic ring. It is of the same order of magnitude as that of the halogens. The −I effect is variable, dependent on the degree of electron withdrawal by the inductive effect of the β-vinyl group.

TABLE I

DETERMINATION OF THE pK_a VALUE OF 4-β-CYANOVINYLPYRIDINE[a]

λ, nm	pH	Optical density d	Log $(d_m - d)/(d - d_i)$	pK_a
255	3.45	0.448	0.66	4.11
	3.78	0.466	0.36	4.14
	4.00	0.480	0.12	4.12
	4.25	0.503	−0.11	4.14
	4.60	0.529	−0.46	4.14
	4.85	0.546	−0.79	4.06
	5.15	0.552	−1.06	4.09
270	3.60	0.538	0.53	4.13
	3.90	0.498	0.15	4.05
	4.15	0.468	−0.09	4.06
	4.40	0.442	−0.31	4.07

pK_a 4.10 ± 0.05

[a] Stock solution, 1.50 × 10^{-3} M in 1% aqueous ethanol (for other compounds stock solution concentrations of up to 25% aqueous ethanol were used, but in all cases analytical solutions contained no more than 1% ethanol); analytical solution, 1.50 × 10^{-4} M; buffer, 0.01 M acetic acid-0.01 M sodium acetate; analytical wavelengths, 255 and 270 nm; optical density of free base (d_m), 0.566 (255 nm), 0.370 (270 nm); conjugate acid (d_i), 0.422 (255 nm), 0.588 (270 nm).

TABLE II

pK_a DETERMINATIONS

Compd	λ_{max}, nm FB[a]	λ_{max}, nm CA[b]	Method of pK_a detn[c]	Analytical wavelengths, nm	pK_a, 25°
Pyridine	253	255	S	245, 255	5.14[d]
			P		5.13[d]
3f	286	275	S	275, 310	4.05
2f	250	252	S	250	4.83
3g	275	283	S	285	4.25
2g	278	283	S	280, 285	4.82
3e	258	254	S	225	4.02
2e	259	271	S	230, 270	4.96
3d	272	262	S	275, 285	3.88
2d	263	257	S	225	5.19
3b	258	255	S	210, 220, 225, 230	3.69
2b	258	269	S	255, 270	4.10
3a			P		3.44
3c	290	266	S	285, 295	3.71
2c	267	274	S	250, 255, 285	4.33
4-Vinylpyridine	242	265	S	230	5.61
5b	223	222	S	230, 235	4.13
5a	266	271	S	275, 280, 285, 290	4.29
			P		4.34[e]

[a] Free base. [b] Conjugate acid. [c] S, spectrophotometric; P, potentiometric. [d] These values are well within the range reported by other workers; see A. Pietryzyk, R. Wiley, and D. McDaniel, *J. Org. Chem.*, **22**, 83 (1957). [e] Considered less accurate than spectrophotometric determination.

This description may well be the *only* conclusion of genuine significance which can be attached to the results. Nevertheless, it is tempting to define these interactions by a further dissection of the σ values, even if there is some controversy and doubt regarding the validity of such a process,[22] particularly in this case where only a small range of substituent effects is being considered.

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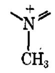
(15) J. M. Essery and K. Schofield, *J. Chem. Soc.*, 2225 (1963).

(16) It is surprising that pK_a values of pyridine correlate with σ and not σ^+. Perhaps the answer lies in the fact that electron deficiency in the pyridinium ion arises in the N sp^2 orbital which is orthogonal to the p-orbital aromatic system responsible for communication of substituent resonance effects. This situation is different from that of the transition state for solvolysis of *tert*-cumyl chlorides, where the deficit occurs in a p orbital overlapping with the aromatic system, or for electrophilic substitution, where it arises directly in the p orbitals whose interaction is responsible for aromaticity in the ground-state molecule. Some support is given for this from the work of Blanch[17] and Miller.[18] The reaction rate of 4-chloropyridine with sodium methoxide affords a σ^- value for the substituent **10** of 2.32. The σ value for **11** from the ionization of 4-pyridinecarboxylic acid is 2.34;



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11

clearly in this case the positive nitrogen cannot avail itself of additional resonance interaction with excess of negative charge. Conversely, however, the second pK_a's of 3- and 4-aminopyridine do reveal an exalted value in the second case, 4.0.[19]

Moreover this reasoning would suggest that, while the correlation of the pK_a's of pyridine N-oxides[20] with σ^- is explicable in that the system is isoelectronic with phenolate anion, that with σ^+ is not. This latter anomaly might be clarified by further quantitative experiments involving electrophilic reaction at the oxygen atom of such compounds, and incorporation of data in an equation of the Yukawa–Tsuno type[21]

$$\log k/k_0 = \rho[\sigma + r(\sigma^+ - \sigma)]$$

Thus, it is noteworthy that the latter workers report a value of r of 0.55 rather than ~1 for the σ^+ correlation with pK_a values of pyridine N-oxides. Clearly there is much that is not yet fully understood in the application of Hammett-type equations to heteroaromatic systems.

(17) J. H. Blanch, *J. Chem. Soc. B*, 937 (1966).

(18) M. Liveris and J. Miller, *ibid.*, 3486 (1963).

(19) H. H. Jaffé and H. Lloyd Jones, *Advan. Heterocycl. Chem.*, **3**, 209 (1964).

(20) H. H. Jaffé, *J. Org. Chem.*, **23**, 1790 (1958).

(21) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jap.*, **39**, 2274 (1966).

(22) See in particular M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 421.

TABLE III

HAMMETT SUBSTITUENT CONSTANTS

Substituent ⫽\X	σ^a	X σ_I (arom)[b]	 σ_I (nmr)[b]
3-CH=CHCOC$_6$H$_5$	0.18	0.30[f]	0.20[h]
4-CH=CHCOC$_6$H$_5$	0.05		
3-CH=CHCOC$_6$H$_4$NO$_2$	0.15		
4-CH=CHCOC$_6$H$_4$NO$_2$	0.05		
3-CH=CHCOOC$_2$H$_5$	0.19	0.34	0.21
4-CH=CHCOOC$_2$H$_5$	0.03		
3-CH=CHCOCH$_3$	0.21	0.32	0.23
4-CH=CHCOCH$_3$	−0.01		
3-CH=CHCN	0.24	0.52	0.53
4-CH=CHCN	0.17		
3-CH=CHNO$_2$	0.28, 0.32[c]	0.68	0.60
4-CH=CHNO$_2$	0.26[c]		
3-CH=CHCHO	0.24	0.33[g]	0.31
4-CH=CHCHO	0.13		
3-CH=CH$_2$	0.08,[d] 0.05[e]	0.00	0.00
4-CH=CH$_2$	−0.08,[d] −0.08, −0.08[e]		

[a] Calculated using $\rho = 6.01$, log $K_0 = 5.14$. [b] Taken from Table I, ref 26. [c] Reference 7. [d] Calculated using $\rho = 1.00$, log $K_0 = -4.21$. [e] See reference in footnote *d*, Table II. [f] Calculated from $\sigma_m = 0.34$, $\sigma_p = 0.43$: W. N. White, R. Schlitt, and D. Gwynn, *J. Org. Chem.*, **26**, 3613 (1961). [g] Calculated from $\sigma_m = 0.36$, $\sigma_p = 0.43$: A. A. Humffray, J. J. Ryan, J. P. Warren, and Y. H. Yung, *Chem. Commun.*, 610 (1965). [h] R. G. Pews, Y. Tsuno, and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 2391 (1967), for methylene chloride solvent; the others are for weakly protonic solvents.

The most generally used procedure is that of Taft,[23] who considers that σ values may be parameterized into inductive and resonance components according to the equations

$$\sigma_m = \sigma_I + \alpha\sigma_R \quad (1)$$

$$\sigma_p = \gamma\sigma_I + \sigma_R \quad (2)$$

Theoretically very similar procedures involving the basic assumption of additivity of mutually independent inductive and resonance effects have been proposed by Yukawa and Tsuno[21] and Swain and Lupton.[24] Equations 1 and 2 have been employed in Table III for evaluation of σ_I values for CHO and COC$_6$H$_5$, using $\gamma = 1$ and $\gamma = 0.29$.

Corresponding application of these equations to the *m*- and *p*-vinylbenzoic acid pK_a values (Table III), taking the value for σ_m as 0.08, yields $\sigma_I = 0.15$ and $\sigma_R = -0.23$ for the vinyl substituent. These results may be compared with those for the ethynyl group ($\sigma_I = 0.20$, $\sigma_R = +0.03$) which is thus seen to have a similar electron-withdrawing capacity by induction, but a negligible resonance interaction.[11,25]

Equations 1 and 2 may be modified to (3) and (4) to accommodate the effect of the substituent considered here on the pyridinium ion–pyridine equilibrium

$$\sigma_m = \sigma_I/\beta(\beta \text{ substituent X}) + \sigma_I(\text{vinyl}) + \alpha\sigma_R(\text{vinyl}) \quad (3)$$

$$\sigma_p = (\gamma/\beta)\sigma_I(\beta \text{ substituent X}) + \sigma_I(\text{vinyl}) + \sigma_R(\text{vinyl}) \quad (4)$$

assuming the vinyl group contributes a constant + M effect independent of the variable −I effect of the β substituent, X. The σ_I values are taken from Ritchie and Sager's compilation.[26] A list of three different σ_I values are given arising from various modes of estimation, although all generally are similar for a given substituent as theory demands. However, the values are sufficiently different to enable improvement of a correlation by a judicious selection, a difficulty often arising with the use of modified forms of the Hammett equation, particularly when dealing with a set of effects of limited range as here. We have chosen to use σ_I(arom), because these values can be calculated from σ_m and σ_p values as described previously (see Table III), together with σ_I(nmr).

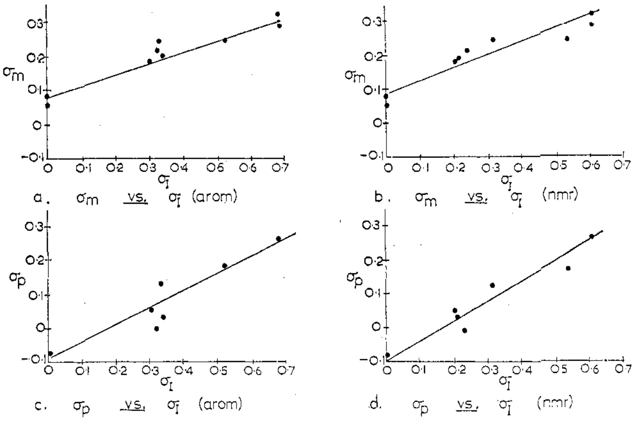

Figure 1.—Correlation of σ (CH=CHX) with σ_I (X).

From eq 3, a plot of σ_m against σ_I for the β substituent should be a straight line of slope β^{-1}. Figure 1a shows such a plot, which gives a straight line of correlation coefficient (r) 0.9585, "satisfactory."[27] The value of β^{-1} is a measure of the reduction factor involved in transmission of the inductive effect of the β substituent through the double bond. This has been given previously as 0.21;[7] the value here is 0.34. The equivalent plot using σ_I(nmr) values has slope 0.35 (r = 0.9331 "fair,"[27] Figure 1b).

The value for γ in eq 4, the factor by which the effect of induction varies between the meta and para positions, is usually taken as unity. From (4), a plot of σ_p *vs.* σ_I should thus be a straight line and have the same slope as the plots in Figure 1a and b passing through the *y* axis at the σ_p value for vinyl. The straight-line correlation of σ_p *vs.* σ_I(arom) (Figure 1c) has a slope of 0.51, r = 0.9248 "fair,"[27] which becomes 0.54, r = 0.9567, "satisfactory,"[27] when σ_I(nmr) values are used (Figure 1d).

The correlation of the σ_m and σ_p values to eq 3 and 4 is thus by no means precisely quantitative, but perhaps it is not too optimistic to say that the measure of correlation is encouraging and probably as good as can be expected considering the overall small range of the substituent effects considered, the theoretical approximations involved, and experimental errors.

The discrepancy between the predicted slope, 0.3, and that calculated, 0.5, for eq 4 could arise from a value of γ greater than unity, a circumstance which has been argued for by Exner[28] for benzenoid systems, but

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[25] C. Eaborn, A. R. Thompson, and D. R. M. Walton, *J. Chem. Soc. B*, 859 (1969).

[26] C. D. Ritchie and W. F. Sager *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

[27] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); however, see J. Shorter, *Chem. Brit.*, **4**, 269 (1968).

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considered unlikely by other groups of workers[24,29] because it places undue emphasis on the I_π effect. Indeed, Swain and Lupton[24] believe the value should be less than 1, which is certainly true for the correlation of pK_a values[8] and rates of quaternization of substituted pyridines.[30] As already noted, Fischer and Vaughan have shown that electron-withdrawing groups of potential (−I, −M)-type exert only a −I effect in these series, a conclusion amply supported by the work of Schofield,[15] and yet all such groups have a different effect depending on whether they occupy the 3 or 4 position (Table IV).

TABLE IV

σ_I VALUES FOR SUBSTITUENTS IN THE PYRIDINE SERIES

Substituent	(i) σ_I (pK_a values[a]) 3	4	3/4	(ii) σ_I (quaternization[b]) 3	4	3/4
CN	0.64	0.55	1.17	0.62	0.52	1.19
NO_2	0.67	0.63	1.07			
$COOCH_3$	0.35	0.28	1.25			
COC_6H_5	0.33	0.31	1.06	0.30	0.23	1.30

[a] Reference 8. [b] Reference 30.

Another explanation of the increased slope of the σ_p correlation could be a competition between the pyridinium nucleus and the β-vinyl substituent for the π electrons of the double bond, which the former always wins but in varying degrees, so that the assumption of a *constant* negative σ_R(vinyl) value in eq 3 and 4 is incorrect. However, $\sigma_R{}^0$ measurements for the β substituents[31] (NO_2, $\sigma_R{}^0 = 0.17$; CN, 0.09; COOEt, 0.18; $COCH_3$, 0.22; CHO, 0.24; COC_6H_5, 0.19) show that the −M effect is not proportional to the −I effect for such substituents. Thus to explain the different slope by this phenomena would involve postulation of interaction between the resonance effect of the vinyl group and the inductive effect of the β substituent, a type of interaction previously suggested[31] and also implicitly assumed,[32] but not widely considered, the mutual independence of M and I effects being the general basis for dual substituent parameter correlations.

Stewart and Walker[7] have measured $\sigma_p{}^-$ for the β-nitro vinyl group; it is 0.88. Clearly, for this substituent, and presumably for the others studied here, the −M effect of the β substituent fully reasserts itself as expected when conjugation with excess of electronic charge is possible. Thus, these groups fall into the small category of those that have both σ^+ and σ^- values significantly different from σ. The sign of the $\sigma_R{}^0$ values of such groups, measured as 0.13 for $CH{=}CHNO_2$ and 0.10 for $CH{=}CHCOOH$,[31] therefore appears to be in some doubt.

Registry No.—**2b**, 24490-79-7; **2c**, 26505-36-2; **2d**, 10416-53-2; **2e**, 24489-96-1; **2f**, 16208-85-8; **2g**, 28430-32-2; **3a**, 3156-52-3; **3b**, 6443-86-3; **3c**, 28447-15-6; **3d**, 28447-16-7; **3e**, 28447-17-8; **3f**, 4452-13-5; **3g**, 28430-33-3; **5a**, 1075-49-6; **5b**, 28447-20-3; **4** vinylpyridine, 100-43-6.

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Mechanisms of Substitution Reactions at Sulfinyl Sulfur. VI. The Kinetics of the Reaction of Mercaptans with Aryl Sulfinyl Sulfones[1]

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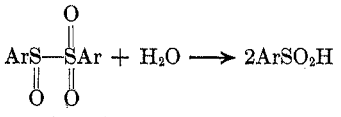
The kinetics of the reaction of *n*-butyl mercaptan with *p*-toluenesulfinyl *p*-tolyl sulfone (**1a**) in 60% dioxane containing 0.001–0.40 *M* perchloric acid have been investigated. In the region 0.001–0.01 *M* $HClO_4$, reaction of $n\text{-}BuS^-$ with **1a** is an important contributor to the rate. At higher acidities the only important contributor to the rate is a reaction between the undissociated mercaptan and **1a**. Reaction of *n*-BuSH with **1a** is not subject to significant acid catalysis, in marked contrast to the butyl sulfide catalyzed hydrolysis of **1a** where nucleophilic attack of $n\text{-}Bu_2S$ on **1a** occurs only if there is accompanying acid catalysis. This difference in the behavior of *n*-BuSH and $n\text{-}Bu_2S$ provides evidence of the probable correctness of the explanation advanced earlier[3] for why acid catalysis is necessary in the sulfide-catalyzed hydrolysis but not in the ordinary hydrolysis of **1a**.

In acidic aqueous dioxane the hydrolysis of aryl sulfinyl sulfones (eq 1) can be markedly catalyzed by the addition of small concentrations of alkyl sulfides such as *n*-butyl sulfide.[3] While the ordinary hydrolysis of **1** under these conditions is *not* subject to acid catalysis, *i.e.*, rate = $k_h(\mathbf{1})$, the sulfide-catalyzed hydrolysis occurs *only* with acid catalysis, *i.e.*, rate = $k_s(H^+)(R_2S)(\mathbf{1})$. To explain this difference in behavior it was suggested[3] that uncharged nucleophiles like H_2O and R_2S are unable to displace sulfinate ion ($ArSO_2^-$) as such from **1**. In the sulfide-catalyzed hydrolysis (eq 2), if R_2S is to effect a substitution on the sulfinyl group of **1**,



$$ArS(=O)\text{—}S(=O)_2Ar + H_2O \longrightarrow 2ArSO_2H \qquad (1)$$

1

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(1) (a) This research was supported by the National Science Foundation, Grant GP-10732X. (b) Preceding paper in this series: J. L. Kice and G. Guaraldi, *J. Org. Chem.*, **33**, 793 (1968).

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