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## The Correlation of the Electronic Spectra and Acidity of 4-Substituted 2-Nitrophenols with Substituent Constants

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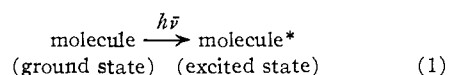
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The apparent  $pK_A$ 's at 25° of a series of thirteen 4-substituted 2-nitrophenols have been quantitatively related to Hammett's  $\sigma$ -values. A theoretical relation between the wave number shift ( $\nu_B - \nu_A = 1/\lambda_{\max}^{\text{N}^{\text{OH}}} - 1/\lambda_{\max}^{\text{H}^{\text{O}}} = \Delta\nu$ ) and  $pK_A$  has been derived from general thermodynamic principles,  $\Delta\nu = -(2.303 RT/2.859) pK_A + (\Delta E^* - T\Delta S^\circ)/2.859$ , where  $\Delta E^*$  is the difference in energy of the excited states, and  $\Delta S^\circ$  is the difference in entropy of the ground states. The deviations in the experimental plot of  $\Delta\nu$  vs.  $pK_A$  are discussed. The wave-number shift,  $\Delta\nu$ , does not correlate well with  $\sigma$ , but  $\nu_B$  and  $\nu_A$  have been correlated separately with  $\sigma^-$ -values. An excellent correlation between  $\nu_B$  and  $\nu_A$  has been found, and the quantitative relation between them has been used to assign structures to equivocal absorption maxima in the spectra of 4-amino-2-nitrophenol and 4-carboxy-2-nitrophenol. Some general considerations in the correlation of electronic spectra with substituent effects are discussed. The experimental evidence suggests that in the ground state there is no interaction between the 4-substituent and the 2-nitro group, but that such interaction does exist in the excited state.

### Introduction

The thesis that substituent effects which influence chemical reactivity similarly affect certain electronic transitions remains to be unequivocally established. In chemical rate processes, energy differences between ground and transition states (or, in equilibria, between initial and final ground states) are considered. In electronic spectral excitations, energy differences between ground and excited electronic states are involved. Although Hammett substituent constants,  $\sigma$ , are empirically derived from chemical reactivities, on the assumption that they are proportional to substituent-induced changes in electron density,  $\sigma$ -values have been correlated with electron densities calculated by molecular orbital theory.<sup>2a</sup> Recently, the differences ( $\Delta\nu$ ) between wave-numbers of visible spectra of neutral and alkaline solutions of 2,4-dinitrophenylhydrazones<sup>3,4</sup> have been shown to be quantitatively related to Hammett and Taft<sup>5</sup> substituent constants for a wide range of substituents. In view of the successful spectra-structure correlations of the 2,4-dinitrophenylhydrazones, it seemed desirable to expand the scope of the study and determine whether the wave number shift,  $\Delta\nu$ , caused by the removal in alkaline solution of the phenolic hydrogen in 4-substituted 2-nitrophenols could also be related to Hammett's  $\sigma$ -constants and the  $pK_A$  values for the nitrophenols. Accordingly, the  $pK_A$ 's and the absorption spectra of a series of 4-substituted 2-nitrophenols in acidic and alkaline media have been measured. The experimental data are recorded in Table I.

If it be assumed that, under certain conditions, the absorption of energy,  $h\nu$ , by a molecule in the ground state may be analogous to chemical reactivity, as formally expressed in eq. 1, a prime requirement for the establishment of a Hammett-type relationship is that all compounds in the series undergo the same electronic transition.



This is the spectral counterpart of the chemical reactivity requirement<sup>2b</sup> that all members of a given series undergo the same single reaction, and *via* the same mechanism. Failure to isolate a single reaction (or single transition, in spectral correlations) may be the cause of serious deviations from the Hammett equation. Since the extinction coefficient is determined by the size of the absorbing species and by the probability of the electronic transition,<sup>6</sup> for a series of compounds whose overall molecular dimensions do not vary greatly, identical transitions may be indicated when intensities of absorption throughout the series retain the same order of magnitude. The use of  $E_{\max}$ , the largest molar extinction coefficient associated with an absorption band, rather than  $Q$ , the integrated intensity, is justifiable if, in a series of closely related substances, the compared absorption bands have the same shape.<sup>7a</sup> Although  $E_{\max}$  is not related to the energy of a *pure* electronic transition due to association of the electronic state with a large number of vibrational and rotational states,<sup>7b</sup> the deviation,  $\Delta\lambda$ , is likely to be small relative to  $\lambda_{\max}$  itself. No attempt is made here to define the exact nature of the electronic transitions of 4-substituted 2-nitrophenols, which are complicated by the possibilities of ring interaction with three groups, in addition to which the hydroxyl group is conjugated to both the 4-substituent and the 2-nitro group. All absorption maxima recorded in Table I are the longest observed wave lengths, most of which are in the visible region.

### Results and Discussion

An excellent correlation has been obtained between the  $pK_A$ 's and structures of thirteen 4-substituted 2-nitrophenols, as illustrated in Fig. 1. Linear regression analysis<sup>2c</sup> of the data in Table I gives

$$pK_A = 6.89 - 2.16\sigma \quad (2)$$

with a correlation coefficient  $r = -0.992$ , and a standard deviation from regression  $s = 0.14$ .

(6) E. A. Braude in E. A. Braude and F. C. Nachod, editors, "The Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 135.

(7) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955: (a) p. 249; (b) p. 247; (c) p. 290; (d) p. 279.

(1) Abstracted from the research results to be used for the Ph.D. dissertation of M. R., The A. and M. College of Texas.

(2) H. H. Jaffé, *Chem. Revs.*, **53**, (1953): (a) p. 227; (b) pp. 236-238; (c) p. 253; (d) pp. 246-248; (e) p. 199, reaction no. 23a; (f) p. 225; (g) pp. 222-223; (h) p. 230; (i) p. 193.

(3) L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25**, 226 (1960).

(4) L. E. Scoggins and C. K. Hancock, *ibid.*, **26**, in press (1961).

(5) R. W. Taft, Jr., in M. S. Newman, editor, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

TABLE I  
 ACIDITY AND SPECTRAL DATA FOR 4-SUBSTITUTED 2-NITROPHENOLS

No.	4-Subst.	$pK_A^a$	$\lambda_B^b$	$\nu_B^c$	$\times 10^{-3}$	$\lambda_A^d$	$\nu_A^e$	$\times 10^{-3}$	$\Delta\nu^f$	$\sigma_p^g$	$\sigma_p^{*h}$
1	NH <sub>2</sub>	7.81 ± 0.01	477	20,964	4.22	421	23,753	2.36	-2789	-0.426 <sup>i</sup>	-1.3
2	OCH <sub>3</sub>	7.31 ± .02 <sup>j</sup>	455	21,978	5.18	391	25,575	3.11	-3597	-.268	-0.778
3	CH <sub>3</sub>	7.40 ± .01	433	23,095	4.68	368	27,174	2.98	-4079	-.170	-.311
4	NHCOCH <sub>3</sub>	6.78 ± .05	429	23,310	4.17	375	26,667	2.25	-3357	-.015	-.469 <sup>k</sup>
5	H	7.08 ± .02 <sup>l</sup>	414	24,155	4.60	350	28,571	3.07	-4416	.000	.000
6	C <sub>6</sub> H <sub>5</sub>	6.73 ± .01	440	22,727	4.13	378	26,455	2.36	-3728	.009	-.179
7	Cl	6.36 ± .01 <sup>m</sup>	426	23,474	4.68	362	27,624	2.93	-4150	.227	.114
8	COO <sup>-</sup>	6.41 ± .01	406	24,631	4.41	347	28,818	2.71	-4187	.351 <sup>n</sup>	.....
9	NH <sub>3</sub> <sup>+</sup>	.....	..	.....	..	342	29,240	3.19	.....	.485 <sup>o</sup>	.....
10	COOCH <sub>3</sub>	5.40 ± .02	400	25,000	4.48	341	29,326	2.72	-4326	.636	.....
11	COOC <sub>2</sub> H <sub>5</sub>	5.44 ± .02	399	25,063	4.44	341	29,326	2.70	-4263	.678	.....
12	COOH	.....	..	.....	..	339	29,499	2.76	.....	.728	.....
13	N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	5.03 ± .01	399	25,063	4.92	335	29,851	2.98	-4788	.859	.....
14	COCH <sub>3</sub>	5.09 ± .02	398	25,126	4.78	340	29,412	2.76	-4286	.874	.....
15	NO <sub>2</sub>	4.07 ± .02 <sup>p</sup>	p	.....	..	.....	.....	..	.....	1.270	.....

<sup>a</sup> The  $pK_A$ 's are apparent, no correction having been made for the activity of the anion. Thermodynamic corrections are not usually greater than 0.1  $pK_A$  unit (see ref. 6, p. 656) and, as such, exert a relatively minor influence in eq. 2 and 6 in which the effect of structure on acid strength is involved. Average deviations from the mean are reported, and a minimum of four determinations were made for each  $pK_A$ . <sup>b</sup>  $\lambda_B(\mu\mu) = \lambda_{\text{max}}^{\text{OH}}$ . <sup>c</sup>  $\nu_B(\text{cm.}^{-1}) = (1/\lambda_B) \times 10^7$ . <sup>d</sup>  $\lambda_A(\mu\mu) = \lambda_{\text{max}}^{\text{HCl}}$ . <sup>e</sup>  $\nu_A(\text{cm.}^{-1}) = (1/\lambda_A) \times 10^7$ . <sup>f</sup>  $\Delta\nu(\text{cm.}^{-1}) = (\nu_B - \nu_A)$ . <sup>g</sup> Except as noted, all  $\sigma$ -values are from Jaffé, ref. 2g. <sup>h</sup> Ref. 10. <sup>i</sup> Ref. 8. <sup>j</sup> H. Staude and M. Teupel, *Z. Elektrochem.*, **61**, 181 (1957), report  $pK_A = 7.40$  (30°), 7.47 (20°),  $\lambda_B = 458 \mu\mu$ , and  $\lambda_A = 392 \mu\mu$ . <sup>k</sup> Ref. 10b. <sup>l</sup> C. M. Judson and M. Kilpatrick, *J. Am. Chem. Soc.*, **71**, 3110 (1949), report  $pK_A = 7.23$  (thermodynamic); A. I. Biggs, *Trans. Faraday Soc.*, **52**, 35 (1956), reports  $pK_A = 7.21$  (thermodynamic),  $\lambda_B = 420 \mu\mu$ ,  $\lambda_A = 353 \mu\mu$ ; L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **71**, 2416 (1949), report  $\lambda_A = 351 \mu\mu$  and  $\lambda_B = 416 \mu\mu$ . <sup>m</sup> V. E. Bower and R. A. Robinson, *J. Phys. Chem.*, **64**, 1078 (1960), report  $pK_A = 6.46$  (thermodynamic), 6.37 (apparent),  $\lambda_B = 427 \mu\mu$ , and  $\lambda_A = 363 \mu\mu$ . <sup>n</sup> Ref. 9. <sup>o</sup> L. A. Flexser, L. P. Hammett and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2107 (1935), report  $pK_A = 4.10$  (apparent), and  $\lambda_B = 364 \mu\mu$ . <sup>p</sup> The longest observed wave lengths in alkaline and acidic media were shoulders fused to shorter wave length absorption bands. The  $pK_A$  was determined at  $\lambda_B = 361 \mu\mu$ .

In eq. 2, 6.89 is the regression  $pK_A^0$ -value for unsubstituted *o*-nitrophenol, 2.16 is  $\rho$ , Hammett's reaction constant, and  $\sigma$  is the substituent constant. It may be predicted from the behavior of

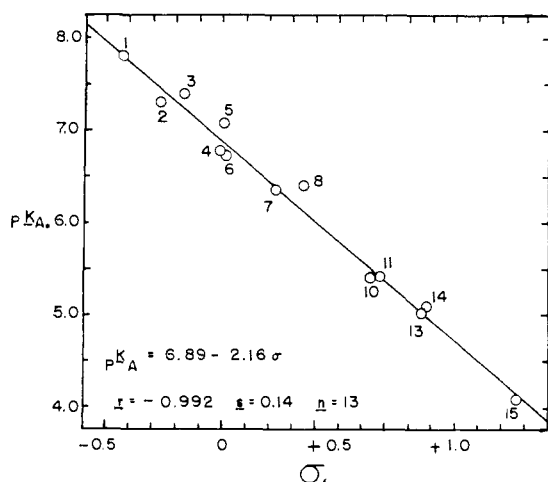
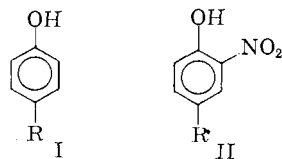


Fig. 1.—The relationship between  $pK_A$  and  $\sigma$  for 4-substituted 2-nitrophenols. Numbers refer to Table I.

other reaction series<sup>2d</sup> that for the  $pK_A$ 's of the two series of phenols, I and II, identical reaction constants,  $\rho$ , should be obtained, provided there is no ground state interaction between the nitro group



and the substituent R. The  $\rho$ -value of  $-2.11^{2e}$  for the  $pK_A$ 's of series I, in excellent agreement with eq. 2, indicates that no such interaction occurs. For electron-withdrawing groups with multiple bonds which are *para* to the hydroxyl group,  $\sigma^-$ -constants, applicable<sup>2f,2g</sup> to the reactions of anilines and phenols, are utilized. The  $\sigma^-$ -value of  $-0.426$  for the *p*-NH<sub>2</sub> group,<sup>8</sup> which correlates closely with the experimental  $pK_A$ , is used rather than the usual value of  $-0.660$ .<sup>2g</sup> Jaffé has suggested<sup>2h</sup> that  $\sigma^-$ -values for electron-releasing substituents in reaction series where the reacting side chain is also electron-releasing, e.g.,  $-\text{OH}$ , should be larger (less negative) than  $\sigma^-$ -values for electron-releasing substituents in reaction series where the reacting side chain is electron-withdrawing, e.g.,  $-\text{COOH}$ . The  $\sigma^-$ -value of 0.351 for the *p*-COO<sup>-</sup> group<sup>9</sup> is used, but in this instance the correlation with the experimental  $pK_A$  is not as good.

A relationship between  $\Delta\nu$  and  $pK_A$  may be deduced from general thermodynamic considerations, independent of the Hammett equation. The difference in energy between ground and excited states,  $\Delta E$  ( $g \rightarrow e$ ), for an electronic transition at a wave length  $\lambda_{\text{max}}$  is

$$\Delta E(g \rightarrow e) = hc(1/\lambda_{\text{max}}) = h\nu \quad (3)$$

where  $h$  = Planck's constant and  $c$  = velocity of light. The energy associated with the wave number difference ( $\Delta\nu = \nu_B - \nu_A$ ), for the basic and acidic forms of the 4-substituted 2-nitrophenols is then

$$hc\Delta\nu = (E_B^* - E_B) - (E_A^* - E_A) \quad (4)$$

where  $E_B^*$  and  $E_A^*$ ,  $E_B$  and  $E_A$ , are the energies of the excited states and ground states of the basic

(8) A. V. Willi and W. Meier, *Helv. Chim. Acta*, **39**, 318 (1956).

(9) A. V. Willi and J. F. Stocker, *ibid.*, **38**, 1279 (1955).

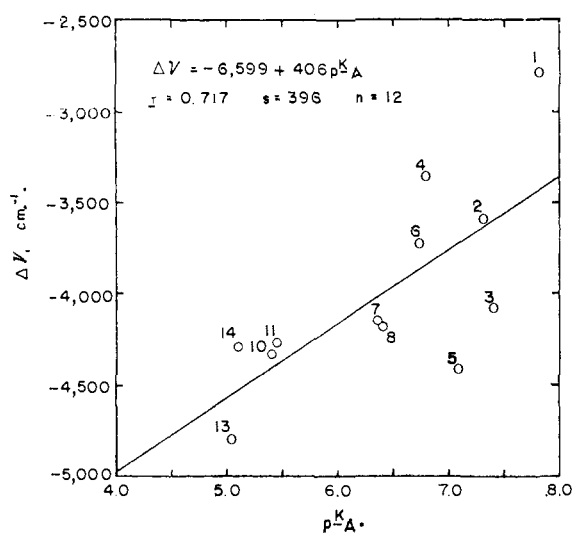


Fig. 2.—The relationship between  $\Delta\nu$  and  $pK_A$  for 4-substituted 2-nitrophenols. Numbers refer to Table I.

and acidic forms, respectively. Equation 4 may be rearranged to give

$$hc\Delta\nu = (E^*_B - E^*_A) - (E_B - E_A) = \frac{\Delta E^* - (\Delta F^\circ - P\Delta V^\circ + T\Delta S^\circ)}{2.859} \quad (5)$$

where  $\Delta E^*$  is the difference between the energies of the excited states in basic and acidic media, and the term  $(\Delta F^\circ - P\Delta V^\circ + T\Delta S^\circ)$  is the difference in energy between the ground states in the same two media, at constant pressure  $P$  and constant temperature  $T$ . The term  $P\Delta V^\circ$ , where  $\Delta V^\circ$  is the change in volume for these neutralization reactions, should not be large and may consequently be ignored. If  $\Delta\nu$  is expressed in  $\text{cm}^{-1}$ , then eq. 5 may be rewritten as

$$\Delta\nu = - \left( \frac{2.303 RT}{2.859} \right) pK_A + \left( \frac{\Delta E^* - T\Delta S^\circ}{2.859} \right) \quad (6)$$

where  $\Delta S^\circ$  is the difference in ground-state entropies,  $R$  is the gas constant expressed in cal./mole/deg., and 2.859 is a conversion factor with units of cal./mole/ $\text{cm}^{-1}$ . If the final term in eq. 6,  $(\Delta E^* - T\Delta S^\circ)/2.859$ , is either constant or has a variation that is small in comparison to the  $pK_A$  term, a plot of  $\Delta\nu$  versus  $pK_A$  at  $25^\circ$  should be linear with a negative slope of about  $-477 \text{ cm}^{-1}$ . Such a plot is illustrated in Fig. 2, and it is interesting to note that a positive slope is obtained by the method of least squares,  $406 \text{ cm}^{-1}$ , which is in complete disagreement with the predicted value. The regression equation for Fig. 2 is

$$\Delta\nu = -6599 + 406 pK_A \quad (7)$$

with  $r = 0.717$  and  $s = 396$ . Although, for 10 d.f., the  $r$ -value of 0.717 is statistically significant at the 0.01 level, the fit is only fair. Several of the  $\Delta\nu$  deviations in Fig. 2 far exceed possible experimental errors in measuring wave number. It thus appears that the final term in eq. 6 is a variable which makes a sizable contribution to the wave number shift. The relationship between  $\Delta E^*$  and  $\Delta S^\circ$  is unknown. Furthermore, the  $\Delta S^\circ$  in eq. 6 need not necessarily be regarded as a constant because of the success of eq. 2.<sup>21</sup> Although  $\Delta S^\circ$  should be small, even slight variations in entropy

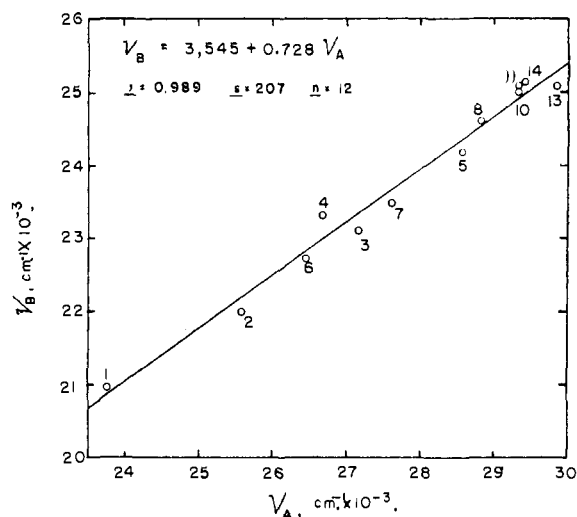


Fig. 3.—The relationship between  $\nu_B$  and  $\nu_A$  for 4-substituted 2-nitrophenols. Numbers refer to Table I.

are magnified in the quantity  $T\Delta S^\circ$ . The  $\Delta E^*$  term in eq. 6 may be evaluated if  $\Delta S^\circ$ , determined from the temperature dependence of the  $pK_A$ , is known. Such  $pK_A$ -temperature studies are now under consideration.

The poor agreement between  $\Delta\nu$  and  $pK_A$  in Fig. 2 may also be rationalized on the basis that, while the  $pK_A$  for 4-substituted 2-nitrophenols is linearly related to  $\sigma$ ,  $\Delta\nu$  appears to be linearly related to the electrophilic substituent constant,  $\sigma^+$ , of Brown and Okamoto,<sup>10</sup> as discussed below. Although  $\sigma^+$ -values for the more strongly electron-withdrawing substituents are numerically similar to  $\sigma$ -values, the  $\sigma^+$ -values for the more strongly electron-donating substituents are much different from  $\sigma$ -values.

An excellent correlation has been obtained between  $\nu_B$  and  $\nu_A$ , the alkaline and acidic wave numbers, respectively, of the 4-substituted 2-nitrophenols, as illustrated in Fig. 3. Linear regression analysis of the twelve conjugate pairs of  $\nu_B$  and  $\nu_A$  values in Table I gives

$$\nu_B = 3545 + 0.728 \nu_A \quad (8)$$

with  $r = 0.989$  and  $s = 207 \text{ cm}^{-1}$ . Apparently, the substituents play identical roles in fulfilling the electron demand requirements of both the  $\nu_B$  and  $\nu_A$  series. Hence, each series may be treated independently with respect to substituent effects in accordance with eq. 1.<sup>11</sup> The  $\nu_B$  and  $\nu_A$  data in Table I for the 4-substituted 2-nitrophenols have been independently and successfully correlated with substituent effects, as illustrated in Fig. 4, provided  $\sigma^+$ -values are used for the more electron-donating substituents. Treatment of the basic wave numbers,  $\nu_B$ , according to the method of least squares gives

$$\nu_B = 23,639 + 1932 \sigma^+ \quad (9)$$

with  $r = 0.967$  and  $s = 367$ . In eq. 9, 1932 is  $\rho^+$ , the spectral reaction constant, and 23,639 is the

(10) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, (1958); (a) p. 4980; (b) p. 4981, reaction G.

(11) W. M. Schubert, J. Robins and J. L. Hahn, *ibid.*, **79**, 910 (1957).

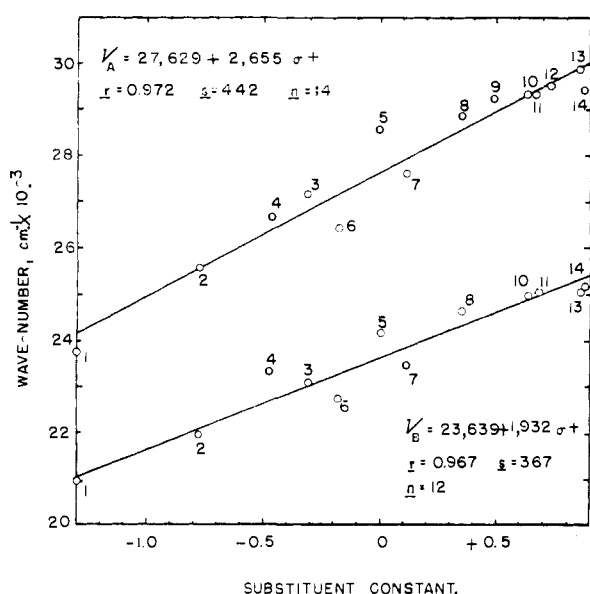


Fig. 4.—The relationship between wave-number and  $\sigma$  ( $\sigma^+$ -values are used where applicable) for 4-substituted 2-nitrophenols. Numbers refer to Table I.

regression value for  $\nu_B^0$ , the alkaline wave number for *o*-nitrophenol. Similar treatment of the acidic wave numbers gives

$$\nu_A = 27,629 + 2655\sigma^+ \quad (10)$$

with  $r = 0.972$  and  $s = 442$ . Attempts to improve eq. 9 and 10 by including a "meta" term,  $\sigma_m^+$ , as an independent variable and submitting the data to multiple regression analysis<sup>12a</sup> did not improve the relations. The "meta" term, introduced because substituent R is *meta* to the nitro group, does not lead to statistically significant improvement. If  $\sigma^+$  from the general form of eq. 10 is substituted into the general form of eq. 9, a linear relation between  $\nu_B$  and  $\nu_A$ , independent of  $\sigma^+$ , is obtained.

$$\nu_B = \left[ \nu_B^0 - \left( \frac{\rho_B^+}{\rho_A^+} \right) \nu_A^0 \right] + \left( \frac{\rho_B^+}{\rho_A^+} \right) \nu_A = 3525 + 0.728\nu_A \quad (11)$$

It is interesting to note that a value of 0.728 is obtained for  $\rho_B^+/\rho_A^+$ , and that a value of 3525 is obtained for the intercept in eq. 11. The agreement between eq. 11 and eq. 8 is striking, indicating that the data in Table I are internally consistent. However, the possibility exists that when correlating  $\nu_A$  and  $\nu_B$  with a variable which does not provide as good a fit as  $\sigma^+$ , e.g.,  $\sigma$ , an equation may be derived similar to eq. 11, e.g., eq. 14, which nevertheless provides a good approximation to eq. 8. Below, computed from the data in Table I, are the regression equations for the correlation of  $\nu_B$  and  $\nu_A$  with  $\sigma$ , instead of  $\sigma^+$ . A comparison of the correlation coefficients and standard deviations of eq. 12 and 13, with those for eq. 9 and 10, suggests that  $\sigma^+$  is the superior independent variable for the correlation of the wave numbers of 4-substituted 2-nitrophenols with substituent constants.

(12) G. W. Snedecor, "Statistical Methods," 5th edition, The Iowa State College Press, Ames, Iowa, 1956: (a) Chapter 14; (b) p. 136.

$$\nu_B = 23,073 + 2797\sigma \quad (12)$$

$$r = 0.915 \text{ and } s = 578$$

$$\nu_A = 26,883 + 3762\sigma \quad (13)$$

$$r = 0.905 \text{ and } s = 802$$

Nevertheless, the values of 0.743 and 3099, calculated for the slope and intercept, respectively, of eq. 14, are in fair agreement with eq. 8. Student's "t"-test<sup>12b</sup> shows no statistically significant difference between these results.

$$\nu_B = \left[ \nu_B^0 - \left( \frac{\rho_B}{\rho_A} \right) \nu_A^0 \right] + \left( \frac{\rho_B}{\rho_A} \right) \nu_A = 3099 + 0.743\nu_A \quad (14)$$

The linear regression equations for  $\Delta\nu$  as a function of  $\sigma^+$ , and for  $\Delta\nu$  as a function of  $\sigma$ , computed from the data in Table I, are

$$\Delta\nu = -3969 - 704\sigma^+ \quad (15)$$

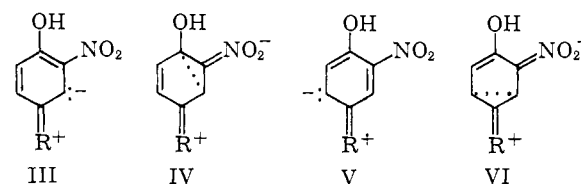
$$r = -0.887 \text{ and } s = 263$$

$$\Delta\nu = -3784 - 930\sigma \quad (16)$$

$$r = -0.766 \text{ and } s = 365$$

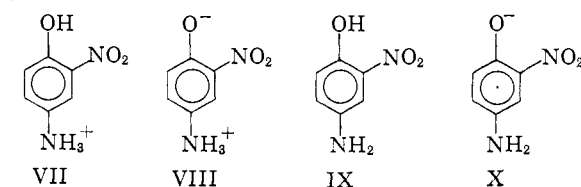
The correlation coefficient,  $r$ , for eq. 15 is smaller than the  $r$ 's obtained for eq. 9 and 10, perhaps because  $\Delta\nu$ , as a relatively small difference between two large numbers, involves greater uncertainties. It should be noted that in using  $\Delta\nu$  (instead of  $\nu_B$  or  $\nu_A$ ) to correlate with substituent constants, the concept implied in eq. 1 is somewhat obscured.

Equations 9 and 10 are consistent with the argument that structures such as III–VI contribute much more to the electronically excited state of the 4-substituted 2-nitrophenols than to the ground state. This agrees with a previous observation<sup>7c</sup> that the visible absorption maxima for the acidic and basic forms of *o*-nitrophenol are closely related to the absorption by benzene itself at shorter wave lengths, and are analogous to the  $N \rightarrow V$  bands<sup>7d</sup> of  $\alpha,\beta$ -unsaturated carbonyl compounds.



The positive  $\rho^+$  of eq. 9 and 10 is consistent with the argument that as the 4-substituent becomes more electron withdrawing, it increases the excitation energy of the transition by producing still greater charge separation in the excited state.

Four species of the 4-amino-2-nitrophenol may exist in solution, as illustrated below. This compound may therefore yield pertinent  $pK_A$  values



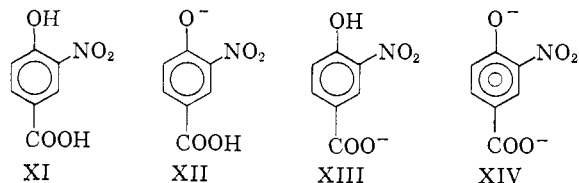
for VII  $\rightarrow$  VIII and IX  $\rightarrow$  X. However, the visible absorption spectrum shows only three peaks and two isosbestic points. The absorption maxima in strongly acidic and strongly alkaline media may unequivocally be ascribed to species VII and X.

Omitting the data for the 4-NH<sub>2</sub> and 4-COO<sup>-</sup> compounds, regression analysis of the remaining data of Table I gives

$$\nu_B = 2877 + 0.751\nu_A \quad (17)$$

with  $r = 0.984$  and  $s = 219$ . Absorption maxima for species VIII and IX, calculated by eq. 17, are 403 and 415 m $\mu$ . The observed intermediate  $\lambda_{\max}$  at 421 m $\mu$  has therefore been ascribed to species IX. The  $pK_A$  for IX  $\rightarrow$  X calculated on this basis and the magnitude of the extinction coefficient at 421 m $\mu$  are also in agreement with the assignment.

Similarly, 4-carboxy-2-nitrophenol shows only three peaks and two isosbestic points, although four possible species may exist. Absorption maxima for species XII and XIII, calculated by eq. 17, are 400 and 345 m $\mu$ .



The observed value for the intermediate peak, 347 m $\mu$ , is therefore assigned to species XIII.

From an over-all viewpoint, the ability of eq. 9 and 10 to correlate absorption frequencies of 4-substituted 2-nitrophenols with structure, in accordance with eq. 1, is quite satisfactory. The standard deviations from regression of 367 and 442 cm.<sup>-1</sup>, respectively, correspond to less than  $\pm 3.5$  m $\mu$  (if the mid-range wave lengths of 437 and 378 m $\mu$  are chosen as reference points for the basic and acidic series). Uncertainties in the values of the substituent constants, as well as experimental error in measurement of wave length, undoubtedly contribute to these standard deviations. However, the rather large deviations of 942 and 516 cm.<sup>-1</sup> for *o*-nitrophenol and *o*-nitrophenoxide ion, for which there can be no uncertainty in substituent constant ( $\sigma = 0.00$ , by definition), do not at all lie in the range of possible experimental error. Perhaps these large deviations reflect the fact that the spectral "reaction" encompasses the entire molecule, an "area" effect, whereas substituent constants are defined for reactions localized at a particular reaction site. Consistent with this is the smaller standard deviation of 207 cm.<sup>-1</sup> (corresponding to less than  $\pm 2$  m $\mu$ ) for eq. 8. Since eq. 8 is devoid of substituent constants, the standard deviation may be attributed largely to experimental inaccuracy.<sup>13</sup> In Fig. 3, the experimental point for hydrogen is not seriously (190 cm.<sup>-1</sup>) displaced from the regression line, perhaps reflecting the possibility that the "area" effect is cancelled (only a proton differentiates the acidic and basic forms, all other things, *e.g.*, solvent participation, being equal). The theoretical significance of the fairly large intercept in eq. 8, 3,545 cm.<sup>-1</sup> (10.1 kcal./mole), remains to be explained. It should be noted that in Fig. 3, the relative separation and order in which the experimental points fall on the regression line is the same as in Fig. 4, where  $\sigma^+$

(13) S. Z. Lewin, *J. Chem. Educ.*, **37**, A475 (1960).

values are used. Two exceptions to the above are the experimental points for hydrogen and phenyl, possibly because in these two groups the operation of the "area" effect is at a maximum.

### Experimental

The 4-substituted 2-nitrophenols which were commercially unavailable were prepared by methods previously reported in the literature, as listed in Table II, and were recrystallized several times from appropriate solvents.

TABLE II

MELTING POINTS OF 4-SUBSTITUTED 2-NITROPHENOLS	M.p., °C. <sup>a</sup>	Lit. m.p., °C.
4-Substituent		
NHCOCH <sub>3</sub>	157-158.5	159 <sup>b</sup>
NH <sub>2</sub>	127-127.5	128 <sup>b</sup>
N(CH <sub>3</sub> ) <sub>3</sub> +I <sup>-</sup>	193 dec.	<sup>c</sup>
CH <sub>3</sub>	35-36	36.5 <sup>d</sup>
OCH <sub>3</sub>	81.5-83	80 <sup>e</sup>
C <sub>6</sub> H <sub>5</sub>	66-67.5	66 <sup>f</sup>
COCH <sub>3</sub>	131-132	132-132.5 <sup>g</sup>
COOH	182-182.5	184 <sup>h</sup>
COOCH <sub>3</sub>	75-76	75-76 (70-71) <sup>i,j</sup>
COOC <sub>2</sub> H <sub>5</sub>	69-70	75-76 (69) <sup>i,j</sup>
Cl	87-88	87 <sup>k,l</sup>
NO <sub>2</sub>	113-114	113 <sup>m,l</sup>
H	45-46	45 <sup>n,l</sup>

<sup>a</sup> Corrected. <sup>b</sup> A. Girard, *Bull. soc. chim.*, [4] **35**, 772 (1924). <sup>c</sup> Prepared by exhaustive methylation of 4-amino-2-nitrophenol with methyl iodide according to the method of R. Pfeiffer and K. Waldmann, *Ber.*, **90**, 2476 (1957). *Anal.* Calcd. for C<sub>6</sub>H<sub>13</sub>IN<sub>2</sub>O<sub>3</sub>: I, 39.16; equiv. wt., 324.13. Found: I, 38.96; equiv. wt., 323.95. <sup>d</sup> R. Brasch and G. Freyss, *Ber.*, **24**, 1960 (1891); L. W. Clemence and G. W. Raiziss, *J. Am. Pharm. Assoc.*, **23**, 536 (1934). <sup>e</sup> T. Takahashi, N. Hattori and M. Suyematsu, *J. Pharm. Soc. Japan*, **65**, 9 (1945). <sup>f</sup> L. C. Raiford and J. C. Colbert, *J. Am. Chem. Soc.*, **47**, 1454 (1925). <sup>g</sup> F. C. Brown, *ibid.*, **68**, 872 (1946). <sup>h</sup> G. W. K. Cavill, *J. Soc. Chem. Ind.*, **64**, 213 (1945). <sup>i</sup> I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, Vol. III, p. 700. <sup>j</sup> Prepared by esterification of 4-carboxy-2-nitrophenol. <sup>k</sup> Ref. *i*, Vol. I, p. 542. <sup>l</sup> Obtained commercially. <sup>m</sup> Ref. *i*, Vol. II, p. 386. <sup>n</sup> Ref. *i*, Vol. III, p. 756.

The absorption spectra were obtained with a Beckman DK-1, double-beam recording spectrophotometer, provided with a thermospacer through which water maintained at 25.00  $\pm$  0.05° was circulated. The instrument was located in a constant-temperature room maintained at 25.0  $\pm$  0.5°. Stock solutions were prepared by weighing the 4-substituted 2-nitrophenols on an analytical balance, and dissolving them in de-ionized water (prepared by passing distilled water through Amberlite MB-1 ion exchange resin) in volumetric flasks. These then were made up to volume in the constant-temperature room, and had an average concentration of about 2  $\times$  10<sup>-4</sup> M. To obtain the spectra in an alkaline medium, aliquots of the stock solution were diluted with 0.1 N sodium hydroxide and, after dilution, the average concentration was about 1  $\times$  10<sup>-4</sup> M. The spectra in an acidic medium were obtained in a similar manner by diluting aliquots of the stock solution with 0.1 N hydrochloric acid. To determine the  $pK_A$ 's, aliquots of the stock solution were diluted with buffered solutions of several different pH values. All final solutions in the three media were of the same dilution. The solutions were manually shaken for 30 seconds prior to filling the 1-cm. quartz cells and the pH of the buffered solution was immediately measured with a Beckman Zeromatic pH meter using standard glass and calomel electrodes. To facilitate the  $pK_A$  determinations, a series of MacIlvaine citrate-phosphate<sup>14</sup> stock buffer solutions, ranging in pH from 3 to 8 were prepared. The  $pK_A$ 's were determined from the absorbances at  $\lambda_{\max}^{\text{NaOH}}$ , the wave length with the higher extinction co-

(14) "Handbook of Chemistry and Physics," 41st edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1959, p. 1715.

efficient, and calculated<sup>15</sup> from the equation

$$pK_A = pH - \log \frac{A - A_1}{A_2 - A} \quad (18)$$

In eq. 18,  $A$  = absorbance of the buffered solution,  $A_1$  = absorbance of the hydrochloric acid solution,  $A_2$  = absorbance of the sodium hydroxide solution, and  $pH$  refers to the  $pH$  of the buffered solution. All  $pK_A$  values re-

(15) H. F. Walton, "Principles and Methods of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1952, p. 271.

ported in Table I are uncorrected for the activity of the anion and hence are apparent rather than thermodynamic (see Table I, Ref. a).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

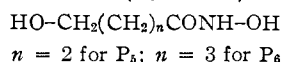
## The Mechanism of the Reaction of Hydroxylamine with $\gamma$ -Butyro- and $\delta$ -Valerolactones. Examples of Reactions Kinetically both Third and Fourth Order

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The reaction of hydroxylamine with  $\gamma$ -butyro- and  $\delta$ -valerolactones in aqueous solution afforded the hydroxamic acids of  $\gamma$ -hydroxybutyric and  $\delta$ -hydroxyvaleric acids via the rate expression  $d \text{ product}/dt = k_1(\text{NH}_2\text{OH})^2(\text{OH}^-)(\text{lactone}) + k_3(\text{NH}_2\text{OH})^2(\text{lactone})$ . The deuterium kinetic solvent isotope effects ( $k^H/k^D$ ) were, for  $k_1$  1.2, and for  $k_3$  2.5. When the hydroxylaminolysis reaction was carried out in the presence of the general base imidazole ( $\text{C}_3\text{H}_4\text{N}_2$ ) the rate expression for the formation of hydroxamic acid was determined to be  $d \text{ product}/dt = k_4(\text{NH}_2\text{OH})^2(\text{OH}^-)(\text{lactone}) + k_3(\text{NH}_2\text{OH})^2(\text{lactone}) + k_{1M}(\text{NH}_2\text{OH})(\text{C}_3\text{H}_4\text{N}_2)(\text{lactone})$ . On the basis of both the solvent deuterium isotope effect and the experiments with imidazole, the general kinetic expression for the hydroxylaminolysis of the lactones is established to involve a mechanism of general base catalysis and a mechanism involving both specific base and general base catalysis.

In aqueous solution at 30° hydroxylamine was found to react with  $\gamma$ -butyro- and  $\delta$ -valerolactones ( $L_5$  and  $L_6$ ) to give, in a quantitative yield, the derived hydroxamic acids ( $P_5$  and  $P_6$ )



Under the conditions of excess hydroxylamine and at  $pH$  values between 6.5 and 8.0 the hydrolysis of  $L_5$  and  $L_6$  was kinetically imperceptible and the rate of hydroxamic acid production and lactone disappearance was found to accurately follow the expression<sup>2</sup>

$$\frac{-dL}{dt} = \frac{dP}{dt} = \left[ k_3(L) + \frac{k_4 K_W}{a_H} (L) \right] \left[ \frac{(N_T) K_A}{K_A + a_H} \right]^2 \quad (1)$$

or

$$dP/dt = k_3(N_F)^2(L) + k_4(N_F)^2(\text{OH}^-)(L) \quad (2)$$

The kinetic expressions for the hydroxylaminolysis of  $L_5$  and  $L_6$  are most unusual in that they contain terms both third and fourth order. In this paper the procedures leading to the establishment of eq. 1-2 and to plausible mechanisms of the reactions are described.

### Results and Discussion

When hydroxylamine is employed in a large excess over  $L_5$  and  $L_6$  and the  $pH$  is constant, the production of  $P_5$  and  $P_6$  is pseudo first order.

$$dP/dt = k_{\text{obs}}(L) \quad (3)$$

If the  $pH$  is kept constant and the value of  $N_T$  varied, then plots of  $k_{\text{obs}}$  vs.  $N_F$  exhibit decidedly up-

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(2)  $N_T$  equals total stoichiometric concentration of hydroxylamine,  $N_F = \text{NH}_2\text{OH}$ ,  $\text{IM}_F$  = free imidazole base,  $\text{IM}_T$  total stoichiometric concentration of imidazole,  $K_W$  = autoprotolysis constant of water,  $K_A = K_1$  = first dissociation constant of hydroxylamine,  $K_2$  = second dissociation constant of hydroxylamine, and  $a_H$  is the hydrogen ion activity as measured by the glass electrode.

ward curvatures. The hydroxylaminolysis reaction with  $L_5$  and  $L_6$  then involves hydroxylamine to more than the first power. The reaction was found to be bimolecular in  $N_F$  by the establishment of a linear relationship between  $N_F^2$  and  $k_{\text{obs}}$  at constant  $pH$ . When reactions were carried out at other constant  $pH$  values, linear plots of  $N_F^2$  vs.  $k_{\text{obs}}$  were invariably obtained, but the pseudo-third-order rate constant ( $k_3'$ ), as obtained from the slopes, were found to vary with  $pH$  (Fig. 1).

$$k_3' = k_{\text{obs}}/N_F^2 \quad (4)$$

Plots of the values of  $k_3'$  vs.  $K_W/a_H$  were linear for both  $L_5$  and  $L_6$  and established the rate expressions 1 and 2 (Fig. 2).

The slopes of the plot of Fig. 2 equal the values of  $k_4$  and the intercepts at  $K_W/a_H = 0$ , equal  $k_3$ . The values so obtained are recorded in Table I.

The question of the mechanistic interpretation of the rate expressions next arose. The fact that the terms of  $k_3$  and  $k_4$  both involve the second power of the hydroxylamine strongly suggested general base-catalyzed mechanisms. If this were so, then, in the presence of the general base imidazole<sup>3</sup> we could have:

**Case I:** General base catalysis only in the  $k_3$  term. Then at any constant  $pH$

$$v = k_{\text{obs}}(L)$$

$$v = k_4(\text{OH}^-)(N_F)^2(L) + k_3(N_F)^2(L) + k_{1M}(N_F)(\text{IM}_F)(L)$$

$$\frac{k_{\text{obs}}}{N_F^2} = k_4(\text{OH}^-) + k_3 + \frac{k_{1M}}{N_F}(\text{IM}_F) \quad (5)$$

and a plot of  $k_{\text{obs}}/N_F^2$  vs.  $\text{IM}_F/N_F$  should be linear with slope  $k_{1M}$  and intercept  $k_4(\text{OH}^-) + k_3$  (i.e.,  $pH$  dependent intercept and  $pH$  independent slopes).

**Case II:** The second hydroxylamine molecule in both  $k_3$  and  $k_4$  terms is involved as a general base

(3) Imidazole was chosen as the general base because its  $pK_A'$  of 7.1 made it about the most effective general base available in the  $pH$  ranges employed in this study.