Spectrophotometric Studies of Some 2,4-Dinitrophenylhydrazones. IV. The pK_a's of *m*- and *p*-Substituted Aromatic Carbonyl Derivatives[1]

LOUIS A. JONES[2] AND NANCY L. MUELLER

Research Laboratories of the Brown & Williamson Tobacco Corporation, Louisville, Kentucky, and the Department of Chemistry, North Carolina State College, Raleigh, North Carolina

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The pK_a's and $\Delta\nu$-values ($\nu_{\max}^{A^\ominus} - \nu_{\max}^{HA}$) in 1:1 dioxane–water (0.40 N in NaX) were determined for thirteen benzaldehyde and twelve acetophenone 2,4-dinitrophenylhydrazones (DNP's). The results gave the following equations when statistically correlated with Hammett σ-values; for benzaldehydes, $-\Delta\nu = 4506$ cm.$^{-1}$ + $1698\ \sigma$ ($r = -0.977$, $s = 198$ cm.$^{-1}$), p$K_a = 10.90 - 0.441\sigma$ ($r = -0.961$, $s = 0.057$); for acetophenones, $-\Delta\nu = 4525$ cm.$^{-1}$ + $1868\ \sigma$ ($r = -0.974$, $s = 223$ cm.$^{-1}$), p$K_a = 11.18 - 0.511\ \sigma$ ($r = -0.985$, $s = 0.044$). The absorption maxima in neutral and basic solutions differed from those previously reported,[1] and the results are discussed in terms of the differences in dielectric constant of the spectral solvent. It is proposed that $\alpha(hc\Delta\nu) = \alpha\Delta\psi = \Delta E_p°$ where $\Delta E_p°$ is the potential energy change in the neutralization reaction, $\Delta\psi$ is proportional to the change in resonance energy stabilization realized in the conversion DNP → DNP$^\ominus$, and α is a proportionality constant characteristic of the reaction series studied. Using thermodynamic principles, the equation $\Delta F° = \alpha\Delta\psi + \Delta E_z° - RT \ln(\pi Q)$ is proposed and the general equation p$K_a = \alpha(2.11 \times 10^{-3}$ cm.) $\Delta\nu$ + C derived. For the DNP's, $\alpha = 0.106$.

The absorption maxima of N-methyl-2,4-dinitrophenylhydrazones[3] do not exhibit the bathochromic shifts of 2,4-dinitrophenylhydrazones (DNP's)[4] when the spectral solvent is changed from neutral to basic solution. It has been proposed that the N-hydrogen of DNP's was acidic under these conditions[3] and further studies appear to support this hypothesis.[5] Spectral studies have since shown that when the absorption maxima in neutral and basic solution are expressed in wave numbers, the difference between these maxima, $\Delta\nu$, can be correlated with the structure of the parent carbonyl compound,[1] *i.e.*, Hammett σ-values[6,7a] for the aromatic DNP's and Taft σ^*-values[8a] for the aliphatic derivatives. The results were discussed in terms of the "free energies" of the reaction DNP + OH$^\ominus \rightleftharpoons$ DNP$^\ominus$ + H_2O, and it was suggested that the ionization constant should be a function of the Hammett σ-values[6,7a] since the $\Delta\nu$-values could be correlated thusly. At that time, however, comparison between pK_a and $\Delta\nu$-values was not possible since only a few DNP pK_a's had been reported[9] and the effect of systematic variation of substituents on the ionization constant had not been investigated. We now report the results of a spectrophotometric determination of the pK_a's of twenty-five *m*- and *p*-substituted benzaldehyde and acetophenone DNP's and the correlations with Hammett substituent constants[6,7a] and $\Delta\nu$-values.

Experimental

The aromatic carbonyl compounds were obtained from commercial sources and, where necessary, purified to agree with published physical constants. The procedure for the preparation of the DNP's has been previously described.[4] Melting point data are contained in Table II.

The pK_a determinations of the DNP's in dioxane–water (1:1 v./v.) were done by a spectrophotometric method similar to that of Biggs.[10] Since a solution 0.40 N in sodium hydroxide was sufficient to convert the weakest DNP to its conjugate base, all solutions were prepared by diluting a saturated aqueous solution of sodium hydroxide such that the total molar concentration of sodium hydroxide plus sodium chloride (reagent grade dried at 60° in a vacuum oven) was 0.40 N in 1:1 dioxane–water. The hydroxide ion concentration was determined by titration of dried reagent grade potassium acid phthalate to the phenolphthalein endpoint and the more dilute solutions were prepared by accurate dilution, sodium chloride being added to maintain a constant molar concentration of 0.40. Dioxane was purified by (1) storing over sodium hydroxide pellets for at least 48 hr., (2) distilling from sodium and collecting the fraction boiling 100–102°, and (3) storing in the dark under nitrogen.

Spectra were obtained on a Cary Model 14 spectrophotometer with 0.40 N sodium chloride in 1:1 dioxane–water in the reference beam at 23 ± 0.3°. DNP solutions were prepared by dissolving approximately 0.025 g. of the derivative, accurately weighed, in 100 ml. of purified dioxane and diluting 2 ml. to 50 ml. with the base solution of the required normality. The solution was shaken and the spectrum from 300–600 mμ recorded immediately. The observed absorbance values obtained at the maximum absorption wave length of the conjugate base were used in the equation

$$\mathrm{p}K_a = \mathrm{pH} + \log \frac{A_{A^\ominus} - A_{\mathrm{obs.}}}{A_{\mathrm{obs.}} - A_{\mathrm{HA}}}$$

where $A_{A^\ominus}$ is the absorbance of the conjugate base in 0.40 N sodium hydroxide, $A_{\mathrm{obs.}}$ is the experimentally observed absorbance at the concentration of base used, and A_{HA} is

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[1] For part III, see L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25**, 226 (1960).

[2] Address: Department of Chemistry, North Carolina State College, Raleigh, North Carolina. To whom inquiries should be sent.

[3] F. Bohlman, *Ber.*, **84**, 490 (1951).

[4] L. A. Jones, J. C. Holmes, and R. B. Seligman, *Anal. Chem.*, **28**, 191 (1956).

[5] L. A. Jones and C. K. Hancock, *J. Am. Chem. Soc.*, **82**, 105 (1960).

[6] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[7] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, (a) p. 188; (b) p. 77; (c) p. 197.

[8] R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13. (a) p. 619; (b) p. 564; (c) p. 567f; (d) p. 666.

[9] C. J. Timmons, *J. Chem. Soc.*, 2613 (1957).

[10] (a) A. I. Biggs, *Trans. Faraday Soc.*, **50**, 800 (1954); (b) R. A. Robinson and A. I. Biggs, *ibid.*, **51**, 901 (1955).

the absorbance of the acid at the conjugate base absorption wave length measured in 0.40 N sodium chloride. The pH was calculated directly from the molar concentration of base since the DNP concentration was approximately 1×10^{-5} M while the lowest concentration of base was 10^{-4} M. Neglecting the amount of base used involved an error of approximately 0.016 pK_a units or less than 10% of the calculated standard deviations. To assure optimum accuracy, only absorbance ratios of DNP$^{\ominus}$/DNP between 0.15 and 0.85 were used, each determination resulting in a minimum of three pK_a values and all samples were determined at least in duplicate. The data used in the calculation of the pK_a of p-nitrobenzaldehyde DNP are shown in Table I and the apparent pK_a's and their standard deviations as well as other constants of all derivatives are shown in Table II. The systematic variation in the pK_a values as indicated by the standard deviations can be partially attributed to the as yet not understood decomposition reaction of DNP's in base.[4]

TABLE I

pK_a DETERMINATION OF p-NO_2-BENZALDEHYDE DNP

$[OH^-]$	$(A_{obs.} - A_{HA})^a$	$(A_{A^{\ominus}} - A_{obs.})^a$	pH	pK_a
0.000	0.000	0.908	....	...
2.26×10^{-4}	.312	.596	10.354	10.63
2.95×10^{-4}	.408	.500	10.470	10.56
3.43×10^{-4}	.499	.409	10.535	10.45
3.95×10^{-4}	.550	.358	10.597	10.41
4.11×10^{-4}	.561	.347	10.614	10.40
4.37×10^{-4}	.606	.302	10.641	10.34
4.74×10^{-4}	.629	.279	10.676	10.32
5.27×10^{-4}	.690	.218	10.722	10.22
3.95×10^{-1}	.908	.000	....	...
			Average	10.42

[a] Absorbance measured at 545 mμ.

Results and Discussion

The absorption maxima of the aromatic DNP's and their corresponding conjugate bases in the dioxane–water solvent system occurred at longer wave lengths than those values previously reported in chloroform[1,4] (Table III). Comparing the λ_{max} in dioxane–water and chloroform, those derivatives substituted with electron-withdrawing groups showed the largest difference in absorption maxima, $\Delta\lambda$, this difference decreasing as the electron-donating capacity of the substituent increased. A notable exception was the 13 mμ difference found for the p-aminoacetophenone DNP. In the basic solution solvents, the differences observed were nearly constant over the range of substituents investigated.

Considering the canonical structures. I, II, and III, the ground state should theoretically receive limited contributions from ionic structures such as I and III; and, conversely, these structures would make large contributions to the electronically excited states of the molecule. It has been shown[11a] that solvents of low dielectric constant (ϵ_{CHCl}

TABLE II

No.	R	M.p., °C. (uncorr.)	λ_{max}^{HA} mμ	$\epsilon \times 10^{-4}$	$\lambda_{max}^{A^{\ominus}}$ mμ	$\epsilon \times 10^{-4}$	$-\Delta\nu^a$	$-\Delta\psi^b$	pK_a^{c}	$\Delta F^{\circ d}$	σ^e
			Physical constants of R—C_6H_4—CHO DNP's								
1	p-NO_2	320–321^f	404	3.30	545	4.05	6403	18.3	10.42 ± 0.17	14.11	+1.270
2	m-NO_2	293–294^f	384	3.06	490	3.55	5617	16.1	10.57 ± .17	14.31	+0.710
3	m-F	266–267^g	385	3.05	479	3.41	5108	14.6	10.79 ± .22	14.61	+ .337
4	p-Br	258–259^h	385	3.08	482	3.50	5245	15.0	10.70 ± .27	14.49	+ .232
5	p-Cl	265–266^i	388	2.66	478	2.92	4860	13.9	10.73 ± .25	14.53	+ .227
6	m-CH_3O	219–220^f	388	2.93	477	3.18	4820	13.8	10.79 ± .09	14.61	+ .115
7	p-F	278–279^j	387	2.95	470	3.24	4596	13.1	10.81 ± .22	14.64	+ .062
8	H	239–240^f	387	3.04	473	3.30	4699	13.4	10.90 ± .19	14.76	.000
9	3,4-$(CH_3O)_2$	258–259^f	400	3.03	474	3.31	3921	11.2	10.92 ± .18	14.79	− .153
10	m-NH_2	275–276^i	391	2.83	472	3.16	4387	12.5	11.01 ± .17	14.91	− .161
11	p-CH_3	238–240^k	390	3.04	472	3.28	4459	12.7	10.99 ± .19	14.88	− .170
12	p-CH_3O	258–259^f	397	3.08	470	3.30	3944	11.3	11.03 ± .14	14.94	− .268
13	p-$(CH_3)_2N$	239–240^f	437	2.99	486	3.51	2298	6.6	11.26 ± .10	15.25	−1.154^l
			Physical constants of R—C_6H_4—CO—CH_3 DNP's								
14	p-NO_2	264–265^f	394	3.07	553	3.35	7282	20.8	10.58 ± 0.22	14.34	+1.270
15	m-NO_2	233–234^f	380	2.73	491	2.87	5933	17.0	10.77 ± .15	14.59	+0.710
16	4-CH_3O-3-NO_2	256–257^m	386	2.75	480	2.75	5080	14.5	10.94 ± .17	14.82	+ .442^n
17	p-Br	231–232^f	385	2.80	478	2.77	5033	14.4	11.09 ± .14	15.02	+ .232
18	p-Cl	239–240^f	387	2.84	477	2.80	4887	14.0	11.05 ± .12	14.97	+ .227
19	p-C_6H_5	242–243^f	392	3.02	480	2.84	4710	13.5	11.22 ± .11	15.20	+ .009
20	H	247–248^f	385	2.65	468	2.52	4635	13.3	11.16 ± .05	15.12	.000
21	m-NH_2	265–266^o	388	2.61	466	2.60	4314	12.3	11.20 ± .14	15.17	− .161
22	p-CH_3	260–261^f	389	2.71	467	2.58	4311	12.3	11.32 ± .07	15.33	− .170
23	3,4-$(CH_3)_2$	255–256^o	389	2.76	467	2.63	4323	12.4	11.33 ± .11	15.35	− .239^n
24	p-CH_3O	227–228^f	394	2.70	468	2.63	4018	11.5	11.25 ± .14	15.24	− .268
25	p-NH_2	265–266^f	416	2.48	470	2.61	2790	8.0	11.57 ± .03	15.67	− .660

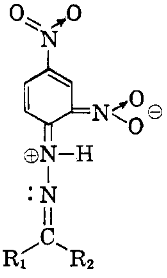
[a] $\Delta\nu = \nu_{max}^{A^{\ominus}} - \nu_{max}^{HA}$. [b] $\Delta\psi = 2.858 \times 10^{-3}\, \Delta\nu$ kcal. mole^{-1}. [c] Apparent pK_a's ± standard deviation. [d] $\Delta F^{\circ} = 2.303\, RT\, \text{p}K_a \times 10^{-3}$ kcal. mole^{-1}. [e] Ref. 6. [f] G. D. Johnson, *J. Am. Chem. Soc.*, **75**, 2720 (1953). [g] Calcd. for $C_{13}H_8N_4O_4F$: N, 18.4. Found: N, 18.2. [h] J. B. Bowen and E. M. Wilkenson, *J. Chem. Soc.*, 750 (1950). [i] N. D. Cheronis and J. B. Entrekin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1957, p. 582. [j] Calcd. for $C_{13}H_9N_4O_4F$: N, 18.4. Found: 18.2. [k] Calcd. for $C_{14}H_{12}N_4O_4$: N, 18.7. Found: N, 18.6. [l] σ-value of −1.154 (ref. 1) used for equation 1 and −0.600 (ref. 6) for equation 4. [m] Calcd. for $C_{15}H_{13}N_5O_7$: N, 18.7. Found: 18.8. [n] σ-value calcd. from ref. 6 as $\sigma_1 + \sigma_2$. [o] Ref. 1.

TABLE III

COMPARISON OF λ_{max} OF DNP'S AND THEIR CONJUGATE BASES IN VARIOUS SOLVENTS

	Dioxane–H_2O[a] λ^1_{max} mμ	Chloroform[b] λ^2_{max} mμ	$\Delta\lambda$[c]	Dioxane–NaOH[d] λ^1_{max} mμ	Alc. NaOH[e] λ^2_{max} mμ	$\Delta\lambda$[c]
			Benzaldehyde DNP's			
p-NO_2	404	381	23	545	537	8
m-NO_2	384	369	15	490	481	9
p-Cl	388	375	13	478	468	10
m-CH_3O	388	369	19	477	469	8
H	387	378	9	473	462	11
m-NH_2	391	381	10	472	467	5
p-CH_3O	397	387	10	470	460	10
p-$(CH_3)_2N$	437	434	3	486	478	8
			Acetophenone DNP's			
p-NO_2	394	382	12	553	540	13
m-NO_2	380	363	17	491	473	18
p-Cl	387	377	10	477	465	12
H	385	377	8	468	461	7
m-NH_2	388	381	7	466	460	6
p-CH_3	389	380	9	467	458	9
3,4-$(CH_3)_2$	389	385	4	467	458	9
p-CH_3O	394	392	2	468	460	8
p-NH_2	416	403	13	470	461	9

[a] Dioxane–water 1:1 (v./v.) 0.40 N sodium chloride. [b] Data taken from ref. 1. [c] $\lambda^1 - \lambda^2 = \Delta\lambda$. [d] Basic solution 0.40 N sodium hydroxide in dioxane–water 1:1 (v./v.). [e] Basic solution 0.25 N sodium hydroxide in ethanol–water 4:1 (v./v.) from ref. 1.



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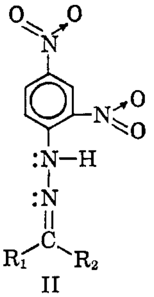

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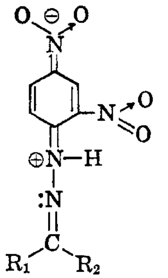
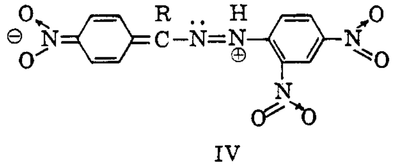


III

4.806)[12] stabilize the nonpolar contributors (in this case II) in the particular energy state in question while high dielectric constant solvents ($\epsilon_{1:1\ \text{dioxane–water}}$ 34.26)[13] lower the excited state energies of the ionic structures (I and III) leaving those of the nonpolar structures unchanged. The decrease in excitation energy due to the latter solvent results in the observed bathochromic shift and the comparatively large $\Delta\lambda$-values obtained for the p-nitro substituted derivatives support the proposal[1] that IV, in addition to I and III, further stabilizes the excited state since the excitation energy is lowered by the solvent of high dielectric constant. The gradual decrease in the $\Delta\lambda$-values as a function of the substituent's electron-donating capacity suggests that the nonpolar structure II becomes more stable relative to the ionic structures I and III as this property increases. The abnormally large $\Delta\lambda$-value for the p-amino group can be ascribed to intermolecular hydrogen bonding with the aqueous medium, thus increasing the stability of the excited state by V.



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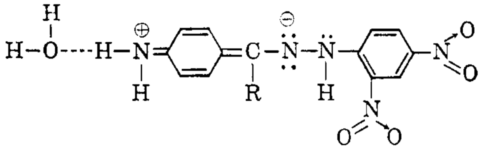

V

Since the p-dimethylamino group cannot engage in such excited state stabilization, a negligibly small bathochromic shift is observed in progressing from a solvent of low dielectric constant to one of high dielectric constant. All the conjugate bases of the derivatives showed essentially the same amount of shift indicating a uniform increase in the stabilization of the excited state of the ion solely due to the large dielectric constant of the dioxane–water solvent system.

$\Delta\nu$-σ Relationships.—The difference $\Delta\nu(\nu^{A\ominus}_{max} - \nu^{HA}_{max})$ of the DNP's and their conjugate bases in chloroform and in alcoholic sodium hydroxide respectively have been previously[1] correlated with aliphatic[8a] and aromatic[6,7a] substituent constants. In view of the differences in λ_{max} observed with a change in solvent (Table III), it seemed desirable to recalculate the $\Delta\nu$-σ relationships.

The substituted benzaldehyde DNP $\Delta\nu$-values were related by the method of least squares[6] to the Hammett substituent constants[6,7a] by the equation,

$$-\Delta\nu = 4506\ \text{cm.}^{-1} + 1698\sigma \qquad (1)$$

with a correlation coefficient r of -0.977 and a standard deviation s = 198 cm.$^{-1}$, the σ-value of -1.154 being used for the p-dimethylamino group.[1] The substituted acetophenone DNP's were similarly analyzed and the equation

$$-\Delta\nu = 4535\ \text{cm.}^{-1} + 2086\sigma \qquad (2)$$

with $r = -0.982$ and s = 198 cm.$^{-1}$ obtained. Combining the data for equations 1 and 2 yielded

$$-\Delta\nu = 4525\ \text{cm.}^{-1} + 1868\sigma \qquad (3)$$

with $r = -0.974$ and s = 223 cm.$^{-1}$. The intercepts of equations 1 and 2 approximate each other more closely than the values previously reported. Although the slope differences are about the same, the dioxane–water system with constant ionic strength serves to decrease the slopes since there is

(11) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955. (a) p. 325ff; (b) p. 353; (c) p. 249; (d) p. 340.

(12) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, Inc., New York, N. Y., 1955, p. 193.

(13) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 118.

no appreciable difference in the dielectric constant in the neutral or basic solution as was the case in changing from chloroform to alcoholic sodium hydroxide.[1]

pK_a-σ Relationships.—Spectra obtained during the spectrophotometric pK_a determinations all contained well defined isosbestic points. Two isosbestic points were exhibited by the acetophenone DNP's, one occurring between the absorption maxima of the DNP and its conjugate base (424–447 mμ) and the other in the range 317–346 mμ. The benzaldehyde DNP's generally showed the former isosbestic point betweeen 425 and 454 mμ and the latter 315–355 mμ. Five of these derivatives (*m*-Cl, *m*-F, *p*-Br, *p*-Cl, and *m*-NH_2) showed no isosbestic point from 300–650 mμ other than that between $\lambda_{\max}^{HA}$ and $\lambda_{\max}^{A\ominus}$ while four derivatives were characterized by a third isosbestic; 3,4-$(CH_3O)_2$ (323 mμ), *p*-CH_3 (312 mμ), *p*-CH_3O (311 mμ), and *p*-$(CH_3)_2N$ (302 mμ).

Benzaldehyde DNP's yielded pK_a's which were found to vary from 10.42 (*p*-NO_2) to 11.26 (*p*-$(CH_3)_2N$) and a statistical correlation between pK_a and Hammett σ-values[6] gave the equation

$$pK_a^B = 10.90 - 0.441\sigma \qquad (4)$$

with $r = -0.961$ and $s = 0.057$. The acetophenone derivatives, pK_a values fell between 10.58 (*p*-NO_2) to 11.57 (*p*-NH_2) and the derived equation[6] was

$$pK_a^A = 11.18 - 0.511\sigma \qquad (5)$$

with $r = -0.985$ and $s = 0.044$. The lines described by the above equations and the experimental points are shown in Fig. 1. The slopes of both lines are very nearly equal suggesting the resonance effects to be the same in the two homologous series, the negative slope indicating the acidity constants increase with electron-withdrawing substituents.

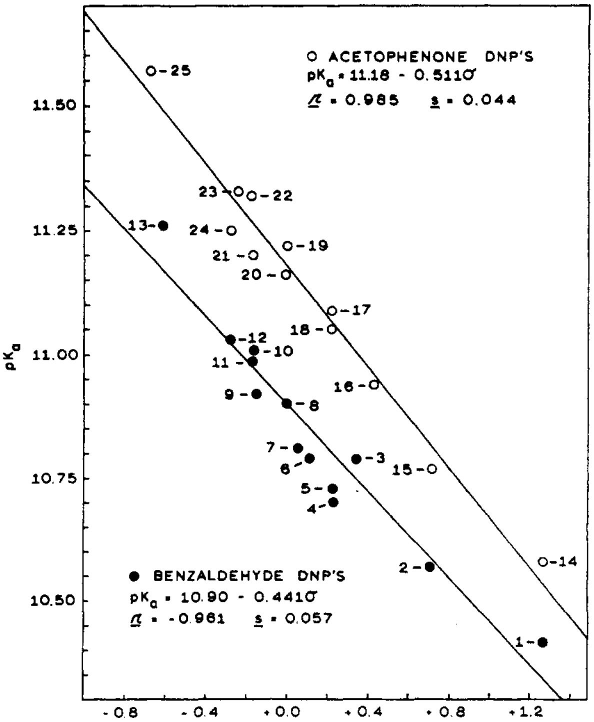

Fig. 1.—Numbers refer to compounds in Table I.

Although there are relatively large changes in $\Delta\nu$ as a function of substituent changes (equation 3), the pK_a-values for the DNP's show only small differences (equations 4 and 5). It seems reasonable that the 2,4-dinitrophenyl group is the determining factor in the pK_a's and that transmission across the —C = N— linkage does not occur with any great facility. The electrostatic interactions of the nitro groups[11b] apparently have a large effect on the resonance (and the spectra) within the DNP's and any modification in the structure of the parent carbonyl compound changes the pK_a only slightly. Apparently $\Delta\nu$-values are more sensitive measures of the acidity of DNP's as previously proposed.[1]

To obtain acceptable precision, it was necessary to use the standard σ-value of -0.600[6] for the *p*-$(CH_3)_2N$ group in the derivation of equation 4 while the value -1.154[1] was used in the $\Delta\nu$-σ relationship. The differences in the σ-values would seem to suggest that the $\Delta\nu$-value is more sensitive to the large electron-donating capacity of the *p*-dimethylamino group, particularly with regard to the stabilization of the ground state of the molecule (*cf.*, ref. 1). Further, the more negative σ-value predicts a larger pK_a value than is actually observed, and the results suggest an acid-strengthening effect not accounted for by the value -1.154.

pK_a-$\Delta\nu$ Relationships.—In absorption spectra, molecules absorb energy and are raised to excited electronic, vibrational, and rotational states which can be related by $hc\nu = E_f - E_i = \Delta E$ where ν is the wave number in cm.$^{-1}$ of light absorbed, E_i and E_f are the initial and final energy states per molecule, respectively, and h is Planck's constant. Approximately, E_i for DNP's can be assumed to include a large weight of II with only minor contributions from I and III while the converse is true for E_f. The total internal energy change of a DNP (HA) is related to the electronic, vibrational and rotational energy changes[14] by

$$\Delta E_{\text{total}}^{HA} = \Delta E_e^{HA} + \Delta E_v^{HA} + \Delta E_r^{HA} = hc\nu_{\max}^{HA} \qquad (8)$$

negligible translational energies being omitted. For the DNP conjugate base, $A^{\ominus}$, a similar relationship applies

$$\Delta E_{\text{total}}^{A^{\ominus}} = \Delta E_e^{A^{\ominus}} + \Delta E_v^{A^{\ominus}} + \Delta E_r^{A^{\ominus}} = hc\nu_{\max}^{A^{\ominus}} \qquad (9)$$

In the DNP and its conjugate base, the only structural difference is the *N*-hydrogen and it would seem reasonable that $\Delta E_v^{HA} + \Delta E_r^{HA}$ should closely approximate $\Delta E_v^{A^{\ominus}} + \Delta E_r^{A^{\ominus}}$, or, if there are differences, these should be linearly related to the substituents. Subtracting equation 8 from 9 gives, under these conditions

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[14] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, D. Van Nostrand, Inc., New York, N. Y., 1951, p. 149.

$$\Delta E^{A^{\ominus}}_{\text{total}} - \Delta E^{HA}_{\text{total}} = \Delta E^{A^{\ominus}}_{e} - \Delta E^{HA}_{e} = hc(\nu^{A^{\ominus}}_{\text{max}} - \nu^{HA}_{\text{max}}) \quad (10)$$

The magnitude of ΔE_e approximates the resonance energy of the molecule[11c,15] and, when ionic forms play an important role in the resonance of the excited state, changes in the ground state can usually be neglected since excited state stabilization is quantitatively more important.[15] The excited state of the DNP$^{\ominus}$, requiring no charge separation, is considerably lower than that of the DNP. Neglecting the relatively small differences in ground state energies, the total energy term in equation 10 reduces to $E_f^{A\ominus} - E_f^{HA}$, hereafter designated as $\Delta\psi$ and defined as a measure of the gain in resonance energy (ψ) which occurs in the DNP–hydroxyl ion reaction.

Fundamental statistical thermodynamics[7b,8b] defines the free energy change as

$$\Delta F^\circ = -RT \ln K = \Delta E_p{}^\circ + \Delta E_z{}^\circ - RT \ln (\pi Q) \quad (11)$$

Basically, $E_p{}^\circ$ contains the potential energy changes arising from polar (σ) resonance (ψ), steric (R), and solvation effects as well as other electrical effects[7b,8c] and thus the total $\Delta E_p{}^\circ = \Delta E_\sigma + \Delta E_\psi + \Delta E_R$.[8d] From the preceding discussion it can be shown that

$$\alpha\Delta\psi = \Delta E_p{}^\circ = \alpha(hc\Delta\nu) \quad (12)$$

where α is a proportionality constant and does not define the fractional contribution of this term to the total potential energy change. Substitution in equation 11 gives

$$\Delta F^\circ = -RT \ln K = \alpha\Delta\psi + \Delta E_z{}^\circ - RT \ln (\pi Q) \quad (13)$$

For a linear relationship to exist between ΔF° and $\Delta\psi$, the term $[\Delta E_z{}^\circ - RT \ln (\pi Q)]$ must either remain constant or vary linearly with $\Delta\psi$. Pending determination of temperature dependence, it is assumed to remain constant and thus

$$\Delta F^\circ = -RT \ln K = \alpha\Delta\psi + C \quad (14)$$

Converting pK_a and $\Delta\psi$ to similar units (Table II) and correlating the data by the method of least squares,[6] for the benzaldehyde derivatives

$$\Delta F^\circ = 0.100\Delta\psi + 16.01 \text{ kcal. mole}^{-1} \quad (15)$$

with $r = 0.949$ and $s = 0.010$. For the acetophenone DNP's,

$$\Delta F^\circ = 0.111\Delta\psi + 16.59 \text{ kcal. mole}^{-1} \quad (16)$$

with $r = 0.965$ and $s = 0.010$. Figure 2 illustrates the lines and experimental points for these equations. The general relationship

$$\text{p}K_a = \alpha(2.11 \times 10^{-3} \text{ cm.})\Delta\nu + C \quad (17)$$

can be derived from 15 and 16 and 2.11×10^{-3} cm. is derived from $Nhc/2.303RT$. The proportionality constant, α, is 0.106 for the DNP's.

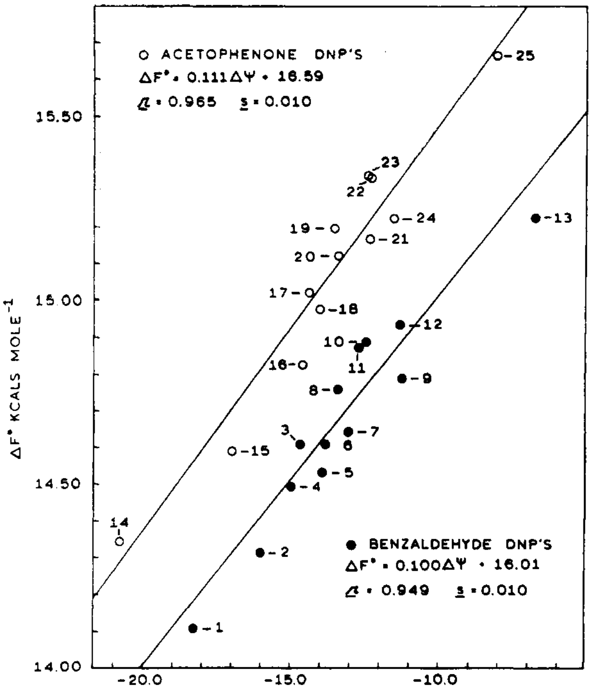

Fig. 2.—Numbers refer to compounds in Table II.

It is proposed that *the proportionality constant α is a measure of the interdependence of changes in the ionization constant and the gain in resonance energy stabilization realized in the conversion of an m- or p-substituted aromatic acid (or base) to its conjugate base (or acid).* Similar to the Hammett ρ[6,7c] in that it is characteristic of the reaction series studied, theoretically (1) α should always be positive since neutralization generally implies a gain in resonance energy stabilization of the product over that of the reactant[11d] and the potential energy changes parallel changes in resonance energy, and (2) α should vary within the limits of zero and one.

The difference in the intercept values of equations 15 and 16 shows the substituted benzaldehyde DNP's to be stronger acids than the corresponding acetophenone derivatives by 0.58 kcal. mole^{-1}. Hyperconjugation and inductive effects of the acetophenone DNP methyl group could conceivably weaken the acid strength relative to the benzaldehyde derivatives and account for this difference. The value of 1.5 kcal. mole^{-1} is usually attributed to hyperconjugation alone.[16]

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