coefficients of the ψ_3 and ψ_4 orbitals reveals a node between carbon and nitrogen in ψ_4 but not in ψ_3. Thus, there is a reduction in the C–N π-bond order on excitation of an electron from ψ_3 to ψ_4.

In summary, the variation of the observed spectral properties of the nitronate anions with their structures is readily interpreted in terms of the model suggested by the molecular orbital calculation. The calculated polarity of the carbonitronate is consistent with that proposed by Pearson and Dillon[13] to account for the pseudo acid and tautomeric properties of nitroalkanes. The bathochromic shift observed with cycloalkanenitronates (Table II) in changing from water to 50:50 dioxane–water is also readily interpretable in terms of the model.

To account for this solvent effect, it is suggested that water molecules are hydrogen bonded to the carbonitronate oxygens.[14] The effect of this bonding can be approximated by increasing the choice of the coulomb integral, δ, of the oxygen. In view of the fact that the orientation of solvent molecules does not change during excitation (Franck–Condon effect), this approach seems justified since the potential field for the π-electrons would be about the same in both the ground and excited states. Thus, if $\delta \geq 1.1$ is a reasonable parameter choice for nonhydrogen-bonded nitronates and hydrogen bonding increases the effective δ, it is seen that increasing δ increases the excitation energy, $\epsilon_4 - \epsilon_3$ (Figure 4). Thus, changing from water to 50:50 dioxane–water should reduce hydrogen bonding and cause the bathochromic shift.[15]

Experimental

Materials.—3,3-Dimethyl-1-nitrobutane was obtained from reaction of 1-bromo-3,3-dimethylbutane and potassium nitrite in DMSO. The nitroalkane was purified by regeneration from its salt and vacuum fractional distillation (b.p. 87° at 41 mm.). Its infrared spectrum showed no absorption bands for functional groups other than the nitro group.

1-Cyclobutynitromethane was obtained from reaction of cyclobutylmethyl tosylate and sodium nitrite in DMF (12% conversion b.p. 97° at 50 mm.). It was converted to cyclobutanecarboxaldehyde by permanganate oxidation of its salt.[17]

Anal. Calcd. for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.12; H, 8.04; N, 12.19.

1-Cyclopropylnitromethane was obtained by oxidation of cyclopropanecarboxaldoxime with peroxytrifluoroacetic acid in acetonitrile.[18] Its salt was converted by the Nef reaction to cyclopropanecarboxaldehyde.[19]

Anal. Calcd. for $C_5H_7NO_2$: C, 47.51; H, 6.93; N, 13.86. Found: C, 47.83; H, 6.89; N, 13.96.

Methods.—Each nitro compound (~0.1 g.) was stirred vigorously until solution was complete in a volume of standard aqueous sodium hydroxide (~0.1 *N*) calculated to give a 10:1 mole ratio of base to the nitro compound. The spectral samples were prepared by diluting aliquots of the alkaline solutions to approximately 10^{-4} *M* in nitro compound. The solutions were handled with minimum exposure to air and analyses were usually completed within 0.5 hr. after preparation of the solutions. The spectra were determined by single-point measurements in a Beckman DU spectrophotometer using 1-cm. silica cells. The shorter wave length measurements on sodium 1-propanenitronate (Figure 5) were determined on a Cary Model 14 spectrophotometer.

Acknowledgment.—The authors wish to thank Mr. Donald Rushmer and Mrs. Loretta Baber for their assistance in the computations.

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[14] Evidence for hydrogen bonding in solutions of nitroalkanes has been given by P. J. Krueger [*Can. J. Chem.*, **42**, 288 (1964)]. Hydrogen bonding to nitronate anions may be expected to be even stronger.

[15] A similar conclusion is reached on the basis of considerations of orientation strain[16] in relation to the expected change (decrease) in the dipole moment of the anion accompanying excitation as estimated from the calculated polarities. This predicts a red shift in changing from water to the less polar dioxane–water solvent.

[16] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 191.

[17] H. Shechter and F. T. Williams, Jr., *J. Org. Chem.*, **27**, 3699 (1962).

[18] An application of the general method of W. D. Emmons and A. S. Pagano, *J. Am. Chem. Soc.*, **77**, 4557 (1955).

[19] Isolated as the 2,4-dinitrophenylhydrazone, m.p. 185–186°, lit. m.p. 186–187.5°: C. L. Wilson, *ibid.*, **69**, 3002 (1947).

The Correlation of the Electronic Spectra, Acidities, and Polarographic Oxidation Half-Wave Potentials of 4-Substituted 2-Chlorophenols with Substituent Constants[1a]

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The electronic spectra, pK_A values, and polarographic oxidation half-wave potentials of a series of 4-substituted 2-chlorophenols (I) have been measured. Correlations of these data have been made and compared with correlations previously reported for a series of 4-substituted 2-nitrophenols (II) and a series of 5-substituted 2-nitrophenols (III). For all three of these series, there are excellent correlations between pK_A and σ, with the ρ value of -2.22 for I agreeing closely with that of -2.16 for II but being much more positive than that of -3.01 for III. As with II and III, there is a good correlation between ν_B and ν_A, but the relationship between $\Delta\nu$ and pK_A is unsatisfactory. Excellent correlations exist between $E_{1/2}$ and σ and between $E_{1/2}$ and pK_A. These and other relationships are discussed.

Recently, it has been shown that there is a quantitative relationship between the basic wave number shifts ($\Delta\nu = \nu_{\max}^{\mathrm{CHCl_3}} - \nu_{\max}^{\mathrm{NaOH}}$) of 2,4-dinitrophenylhydrazones[2,3] and the Hammett[4,5] and Taft[6] substituent constants for a wide range of substituents. A good relationship between the pK_A values and Hammett σ_p values has been established for a series of 4-substituted 2-nitrophenols.[7] A fair correlation between the

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[1] (a) Abstracted from the Ph.D. Dissertation of H. N. S., Texas A & M University, May 1964. (b) To whom inquiries should be addressed.

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

[3] L. E. Scoggins and C. K. Hancock, *ibid.*, **26**, 3490 (1961).

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

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

[6] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

[7] M. Rapoport, C. K. Hancock, and E. A. Meyers, *J. Am. Chem. Soc.*, **83**, 3489 (1961).

Table I

Acidity and Spectral Data for 4-Substituted 2-Chlorophenols

No.	4-Substituent	pK_A[a]	λ_B[b]	ν_B[c]	ϵ_B[d] $\times 10^{-3}$	λ_A[e]	ν_A[f]	ϵ_A[g] $\times 10^{-3}$	$\Delta\nu$[h]	σ_p[i]	σ_p^+[j]
1	NH_2	9.16 ± 0.03	242	41,320	8.64	233	42,920	6.76	−1600	−0.426[k]	−1.3
2	$C(CH_3)_3$	8.58 ± 0.02	239	41,840	6.50	216	46,300	3.90	−4460	−0.197	−0.256
3	$NHCOCH_3$	8.20 ± 0.02	253	38,760	11.8	245	40,820	10.9	−2060	−0.015	−0.469[l]
4	H	8.34 ± 0.03[m]	236	42,370	8.76	213	46,950	7.27	−4580	0.000	0.000
5	C_6H_5	8.07 ± 0.02	285	35,210	19.5	256	39,060	18.4	−3850	0.009	−0.179
6	Cl	7.70 ± 0.01[n]	245	40,820	10.1	218	45,870	7.22	−5060	0.227	0.114
7	Br	7.64 ± 0.01	244	40,980	11.3	218	45,870	8.34	−4890	0.232	0.150
8	COO^-	7.52 ± 0.02	276	36,230	14.9	245	40,820	10.6	−4580	0.351[o]	...
9	NH_3^+	...	...	...	...	216	46,300	6.73	...	0.485[k]	...
10	$COOCH_3$	6.73 ± 0.02	283	35,340	16.2	253	39,530	18.4	−3850	0.636	...
11	COOH	...	...	...	...	255	39,220	12.2	...	0.728	...
12	$N(CH_3)_3^+$	6.62 ± 0.02	*p*	...	...	...	...	...	...	0.770[q]	...
13	NO_2	5.31 ± 0.03[r]	400	25,000	6.69	315	31,746	3.37	−6750	1.270	...
14	Cyclohexyl	8.66 ± 0.03	239	41,840	7.33	217	46,080	5.43	−4240	−0.21[s]	...

[a] The pK_A values are apparent. [b] $\lambda_B (m\mu) = \lambda_{max}^{NaOH}$. [c] $\nu_B (cm.^{-1}) = (1/\lambda_B) \times 10^7$. [d] ϵ_B = extinction coefficient in alkaline solution. [e] $\lambda_A (m\mu) = \lambda_{max}^{HCl}$. [f] $\nu_A (cm.^{-1}) = (1/\lambda_A) \times 10^7$. [g] ϵ_A = extinction coefficient in acid solution. [h] $\Delta\nu (cm.^{-1}) = (\nu_B - \nu_A)$. [i] Except as noted, all σ values are from ref. 5. [j] Ref. 8. [k] A. V. Willi and W. Meier, *Helv. Chim. Acta,* **39**, 318 (1956). [l] Ref. 8. [m] C. M. Judson and M. Kilpatrick [*J. Am. Chem. Soc.,* **71**, 3110 (1949)] report pK_A = 8.48 (thermodynamic); J. W. Murray and N. E. Gordon [*ibid.,* **57**, 110 (1935)] report pK_A = 8.50 (thermodynamic); O. Gawron, M. Dugan, and C. J. Grelecki [*Anal. Chem.,* **24**, 969 (1952)] report pK_A = 8.34 (apparent); lit.[10a] pK_A = 8.53 (thermodynamic). [n] J. W. Murray and N. E. Gordon [*J. Am. Chem. Soc.,* **57**, 110 (1935)] report pK_A = 7.89 (thermodynamic); C. M. Judson and M. Kilpatrick [*ibid.,* **71**, 3110 (1949)] report pK_A = 7.85 (thermodynamic). [o] A. V. Willi and J. F. Stocker, *Helv. Chim. Acta,* **38**, 1279 (1955). [p] The primary absorption band in basic medium could not be determined accurately as it appeared as a shoulder on the slope of a band that appeared at the same point as λ_{max}^{HCl}. The pK_A was calculated at λ_B = 295 mμ. [q] Ref. 10b and 11. [r] V. E. Brown and R. A. Robinson [*J. Phys. Chem.,* **64**, 1078 (1960)] report pK_A = 5.45 (thermodynamic), λ_B = 400 mμ, λ_A = 315 mμ. [s] Calculated by substituting the pK_A value of 8.66 into eq. 1.

pK_A values and the basic wave number shifts ($\Delta\nu = \nu_{max}^{NaOH} - \nu_{max}^{HCl}$) of the 4-substituted 2-nitrophenols was found. Also, ν_{max}^{NaOH} or ν_{max}^{HCl} correlates better with the electrophilic substituent constants, σ^+, of Brown and Okamoto[8] than with Hammett substituent constants.

The pK_A values and absorption spectra of a series of 5-substituted 2-nitrophenols have been measured[9] and a good correlation exists between the pK_A values and Hammett σ_m constants[5]; however, the ρ value of −3.01 for this series is much more negative than that of −2.16 for the 4-substituted 2-nitrophenols.

In view of these successful studies, it seemed desirable to make a similar study of the effect of structure on the acidity and electronic spectra of a series of 4-substituted 2-chlorophenols and to initiate structure–spectra–polarography studies of these and similar compounds.

Results and Discussion

The pK_A values and the ultraviolet absorption spectra of a series of 4-substituted 2-chlorophenols have been measured and the results are shown in Table I. An excellent correlation[5] exists between the pK_A values and Hammett σ_p values for eleven of the compounds as illustrated by Figure 1 and eq. 1. In eq.

$$pK_A = 8.20 - 2.22\sigma_p,\ r = -0.997,\ s = 0.09 \qquad (1)$$

1, 8.20 is the regression pK_A^0 value for unsubstituted 2-chlorophenol, −2.22 is ρ, the Hammett reaction constant, r is the correlation coefficient, and s is the standard deviation from regression. The ρ value of −2.22 in eq. 1 is similar to that of −2.16 found for the pK_A values of 4-substituted 2-nitrophenols.[7] The negative value for ρ indicates that an electron-withdrawing substituent increases the acidity of the respective phenol and this is observed in every case.

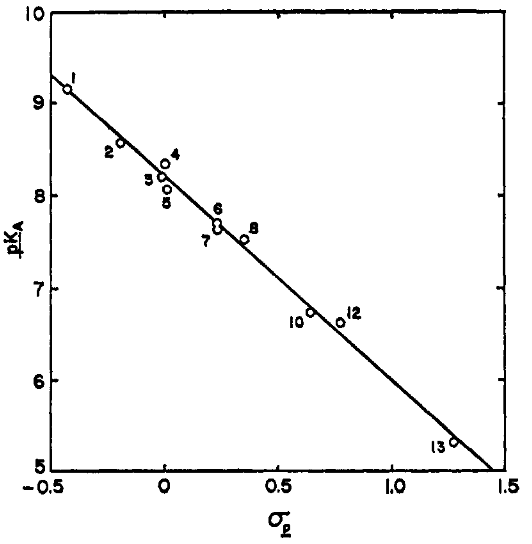
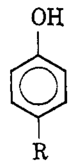
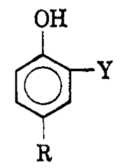


Figure 1.—The relationship between pK_A and σ_p for eleven 4-substituted 2-chlorophenols. Numbers refer to Table I.

Evidence has been cited[5] to suggest that the reaction constant, ρ, is independent of a constant *ortho* substituent. For the two series of phenols, I and II, iden-



I



II

tical reaction constants should be obtained, provided there is no ground-state interaction between the group Y and the substituent R in series II. The ρ value of −2.23 for the pK_A values of series I[10a] is in

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(8) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.,* **80**, 4979 (1958).

(9) C. K. Hancock and A. D. H. Clague, *ibid.,* **86**, 4942 (1964).

(10) (a) A. I. Biggs and R. A. Robinson, *J. Chem. Soc.,* 388 (1961); (b) L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.,* **85**, 3397 (1963).

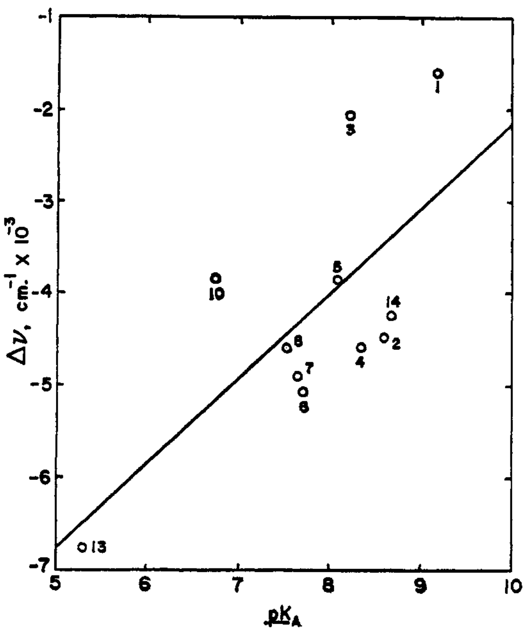

Figure 2.—The relationship between $\Delta\nu$ and pK_A for 4-substituted 2-chlorophenols. Numbers refer to Table I.

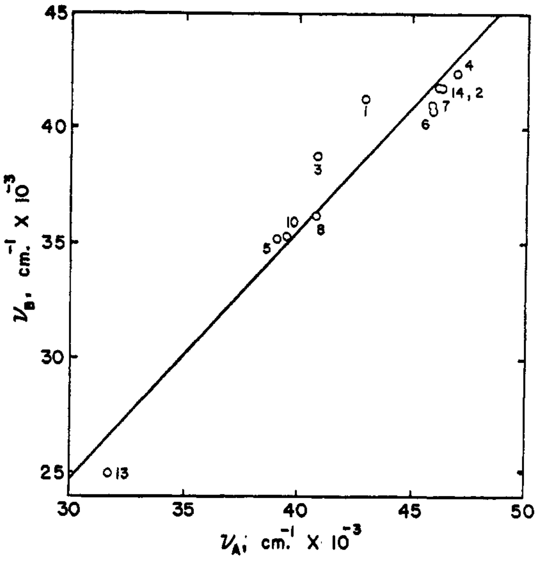

Figure 3.—The relationship between ν_B and ν_A for 4-substituted 2-chlorophenols. Numbers refer to Table I.

excellent agreement with that of eq. 1 and also with that of −2.16 for the series of 4-substituted 2-nitrophenols. The essentially identical reaction constants obtained for these three reaction series indicate that there is no ground-state interaction between the R and Y groups when the R group is *para* to the hydroxyl group. The much more negative ρ value of −3.01 for the series of 5-substituted 2-nitrophenols[9] indicates that there may be interaction between the R and Y groups when the R group is *meta* to the hydroxyl group and *para* to the Y group, since the reaction constants for the pK_A values of *meta*-[11] and *para*-substituted phenols should be about the same.

The regression $pK_A{}^0$ value of 8.20 for the unsubstituted 2-chlorophenol is higher than the regression values reported[7,9] for the unsubstituted 2-nitrophenol. This is as expected since the chloro group is less electronegative than the nitro group and consequently exerts less electron-withdrawing effect on the hydroxyl group.

The σ_p value for the cyclohexyl group was not found in the literature. The value of −0.21 given in Table I was calculated by substituting the pK_A value of 8.66 from Table I into eq. 1.

Ionic substituents are subject to interaction with polar solvents and, as a result, their substituent constants are solvent dependent to a greater extent than are substituent constants for uncharged groups. These solvent interactions can alter the influence of the ionic substituent on the reaction center. The correlation of pK_A with σ_p for the 4-substituted 2-chlorophenols, using a σ_p value of 0.859[5a] for the $N(CH_3)_3{}^+$ group, gives eq. 2. The deviation from

$$pK_A = 8.20 - 2.17\sigma_p,\ r = -0.993,\ s = 0.13 \qquad (2)$$

eq. 2 for the $N(CH_3)_3{}^+$ compound is twice the standard deviation and the ρ value is low compared with that of −2.23 for series I. In view of these reasons, the data were correlated, omitting the data for the $N(CH_3)_3{}^+$ compound, to obtain eq. 3. Equation 1 was obtained by

$$pK_A = 8.20 - 2.23\sigma_p,\ r = -0.998,\ s = 0.08 \qquad (3)$$

including the data for the $N(CH_3)_3{}^+$ compound, using a σ_p value of 0.770.[10b,12] Equations 1 and 3 are essentially identical and the ρ values agree with the ρ value for series I in which no 2-substituent is present.

It has been deduced that there should be a relationship between $\Delta\nu$ and pK_A, and eq. 4 has been derived[7] from general thermodynamic considerations. In eq.

$$\Delta\nu = -\frac{2.303RT}{2.859}pK_A + \frac{\Delta E^* - T\Delta S^\circ}{2.859} \qquad (4)$$

4, ΔE^* is the difference between the energies of the excited states in basic and acidic media, ΔS° is the difference in ground-state entropies, R is the gas constant in cal./mole/deg., and 2.859 is a common factor with units of cal./mole/cm.$^{-1}$. According to this equation, if the last term, $(\Delta E^* - T\Delta S^\circ)/2.859$, is either constant or varies only slightly in comparison to the pK_A term, then a plot of $\Delta\nu$ *vs.* pK_A at 25° should be linear with a negative slope of about −477 cm.$^{-1}$. Such a plot is illustrated in Figure 2 and eq. 5 which

$$\Delta\nu = -11{,}383 + 923pK_A,\ r = 0.696,\ s = 1061 \qquad (5)$$

show considerable disagreement with eq. 4 and the above assumption about the last term. Even though eq. 5 is significant at the 98% confidence level, the slope of 923 is large and *positive* compared to the slope of −477 cm.$^{-1}$ predicted by eq. 4 on the assumption that the last term is essentially constant. Consequently, it appears that the value of $\Delta\nu$ is affected considerably by significant variation of the final term of eq. 4. Probable causes of this variation have been discussed previously.[7] In the above and all subsequent spectral correlations, the data for the $N(CH_3)_3{}^+$ compound are omitted since the primary absorption band in basic medium could not be determined accurately. A large band was found at the same wave length in both acidic and basic media, and an additional band was observed as a shoulder on the large band in basic solution.

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(11) H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).

(12) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

A very good correlation exists between ν_B and ν_A, the basic and acidic wave numbers of the 4-substituted 2-chlorophenols, as illustrated by Figure 3 and eq. 6.

$$\nu_B = -7471 + 1.08\nu_A,\ r = 0.965,\ s = 1425 \qquad (6)$$

This indicates that the ν_A and ν_B series behave similarly with respect to substituent effects.

The correlation between ν_B and Hammett σ_p constants is given by Figure 4 and eq. 7 and that between ν_A and σ_p by Figure 5 and eq. 8.

$$\nu_B = 39{,}776 - 9495\sigma_p,\ r = -0.865,\ s = 2714 \qquad (7)$$

$$\nu_A = 43{,}972 - 6522\sigma_p,\ r = -0.675,\ s = 3422 \qquad (8)$$

Attempts were made to improve eq. 7 and 8 by using other substituent constants. Very good correlations between ν_B or ν_A and the electrophilic substituent constants, σ_p^+, of Brown and Okamoto[8] were obtained for the 4-substituted 2-nitrophenols[7] but the use of σ_p^+ for the 4-substituted 2-chlorophenols gave no improvement. Cohen and Jones,[13] in their study of the spectral properties of hindered phenols introduced a new substituent constant, $\sigma_{R'}$, to better describe the inductive effect of a *meta* substituent. Since the substituent R is *meta* to the chloro group in 4-substituted 2-chlorophenols, the $\sigma_{R'}$ values were calculated and correlated with ν_B or ν_A. The resulting correlations were no improvement over eq. 7 and 8 using σ_p; however, they were better than the correlations using σ_p^+.

The correlation of $\Delta\nu$ with σ_p^+ (better than the correlation with σ_p) is shown in Figure 6 and eq. 9. The

$$\Delta\nu = -4139 - 1905\sigma_p^+,\ r = -0.880,\ s = 741 \qquad (9)$$

σ_p^+ value is numerically similar to the σ_p value for electron-withdrawing substituents but is considerably more negative for electron-donating substituents.

From an over-all viewpoint, the correlation of primary absorption band frequencies of 4-substituted 2-chlorophenols with structure by eq. 7 and 8 is not satisfactory. The standard deviations from regression of 2714 and 3422 cm.$^{-1}$ correspond to about 20 mμ when the mid-range wave lengths of 265 and 243 mμ are chosen as reference points for the basic and acidic series. Such large deviations far exceed the possible experimental error of measuring the wave lengths of the primary absorption bands. The smaller standard deviation of 1425 cm.$^{-1}$ for eq. 6 corresponds to about 10 mμ at a mid-range wave length of 255 mμ. Again, this deviation exceeds the experimental error of measuring the wave lengths of the primary absorption bands. The Beckman DK-1 spectrophotometer used in this study is capable of reproducing the well-defined absorption spectrum of benzene as is shown in the Experimental section. This means that the large deviations from eq. 6, 7, and 8 originate from other sources.

Investigation of the Polarographic Oxidation and Reduction of 4-Substituted 2-Chlorophenols.—Presently available structure–spectra correlations indicate that a relationship of one type may be found for one reaction series while a relationship of a different type may be found for another reaction series. On the other hand, it appears that linear structure–acidity relationships apply in general to these reaction series.

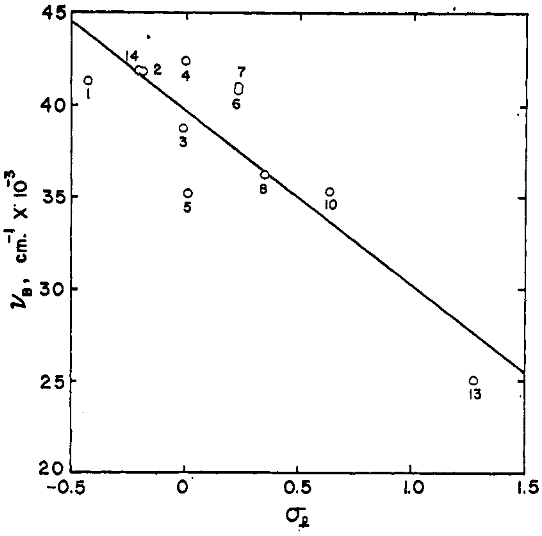

Figure 4.—The relationship between ν_B and σ_p for 4-substituted 2-chlorophenols. Numbers refer to Table I.

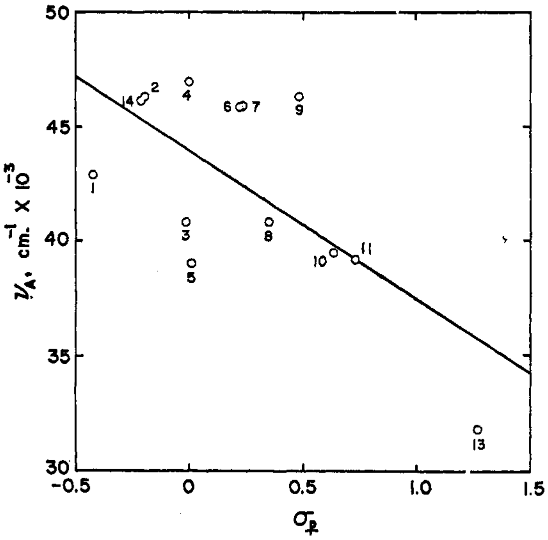

Figure 5.—The relationship between ν_A and σ_p for 4-substituted 2-chlorophenols. Numbers refer to Table I.

Consequently, it seems desirable to investigate some experimental properties which may supply additional information about the ground and excited states. On the basis of a naive molecular orbital (MO) model,[14] in favorable cases, the polarographic oxidation potential is related to the energy of the highest occupied MO of the molecule while the polarographic reduction potential is related to the lowest unoccupied MO. In these favorable cases, the polarographic oxidation potential is related to the energy of the ground state of the molecule while the polarographic reduction potential is related to the energy of an excited state. Thus, the difference in these two potentials is related to the frequency of a spectral transition while the polarographic oxidation potential alone should be related to the ground state energy. In view of the above considerations, polarographic oxidation and reduction studies of the 4-substituted 2-chlorophenols were initiated.

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[13] L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3402 (1963).

[14] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 7.

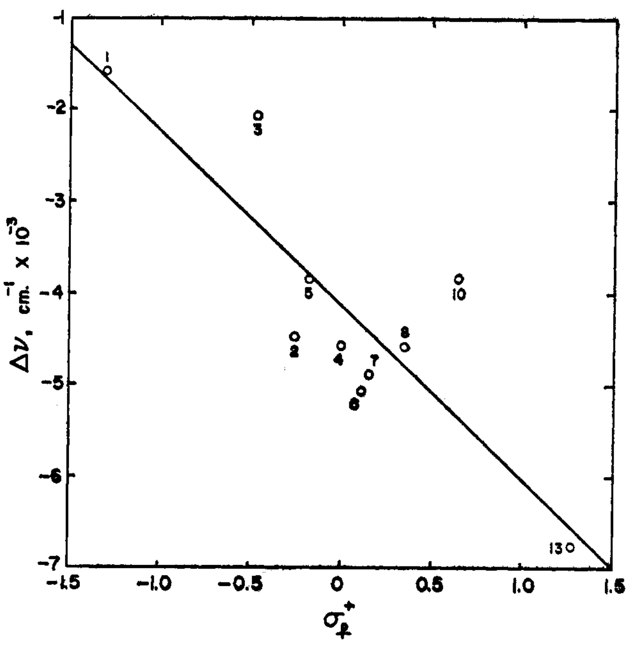

Figure 6.—The relationship between $\Delta\nu$ and σ_p^+ for 4-substituted 2-chlorophenols. Numbers refer to Table I.

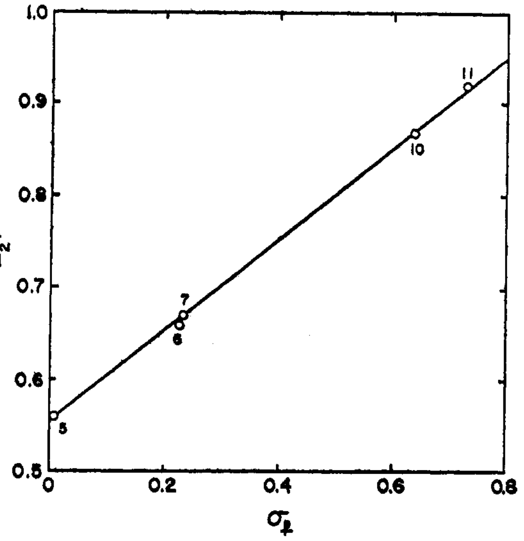

Figure 7.—The relationship between polarographic oxidation half-wave potentials and σ_p for 4-substituted 2-chlorophenols. Numbers refer to Table II.

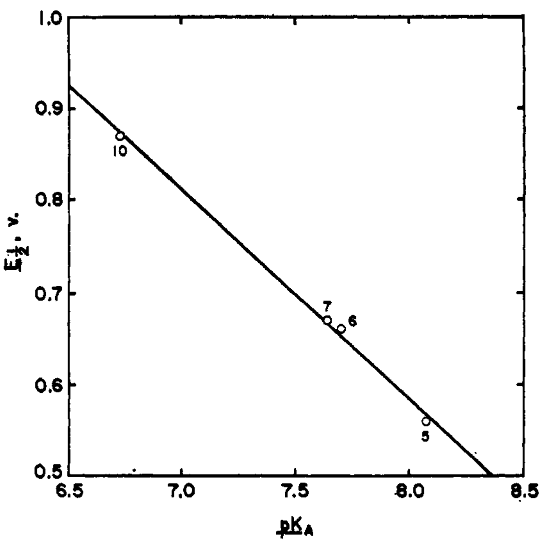

Figure 8. The relationship between polarographic oxidation half-wave potentials and pK_A for 4-substituted 2-chlorophenols. Numbers refer to Table II.

The polarographic oxidation at the rotating platinum electrode was attempted for eight 4-substituted 2-chlorophenols. Oxidation half-wave potentials for five of these compounds are give in Table II. Limitations imposed by the solvent–electrolyte system prevented the measurement of oxidation half-wave potentials for *o*-chlorophenol and 4-*t*-butyl- and 4-nitro-2-chlorophenols. Correlations of the $E_{1/2}$ values from Table II with corresponding σ_p or pK_A values from Table I give eq. 10 and 11 and are illustrated in Figures

$$E_{1/2} = 0.56 + 0.49\sigma_p,\ r = 0.999,\ s = 0.01 \qquad (10)$$

$$E_{1/2} = 2.41 - 0.228\text{p}K_A,\ r = -0.999,\ s = 0.01 \qquad (11)$$

7 and 8. The slope (0.49) of eq. 10 is the reaction constant for the polarographic oxidation of 4-substituted 2-chlorophenols. The positive sign of the slope indicates that electron-withdrawing substituents increase the half-wave potential while electron-releasing substituents decrease the half-wave potential. In terms of the equilibrium constant for the polarographic oxidation, K, eq. 10 becomes

$$\log K^{25°} = \frac{n}{0.0591}E_{1/2} = n(9.5 + 8.3\sigma_p)$$

where n is the number of electrons transferred in the oxidation. In this equation, the ρ value of $8.3n$ is extremely large in comparison to ρ values generally encountered. In eq. 10, the intercept of 0.56 is the regression $E_{1/2}{}^0$ value for unsubstituted 2-chlorophenol. This value agrees with the experimentally estimated value of 0.5 to 0.6 v. which could not be determined accurately because the solvent–electrolyte system has an interfering wave that reaches its limiting current value at about 0.4 v. $E_{1/2}$ values of 1.18 and 0.46 v. calculated by eq. 10 for 4-nitro- and 4-*t*-butyl-2-chlorophenols lie outside the useful range of the solvent–electrolyte system.

TABLE II

POLAROGRAPHIC OXIDATION POTENTIALS OF 4-SUBSTITUTED 2-CHLOROPHENOLS

No.	4-Substituent	$E_{1/2}$ *vs.* s.c.e., v.
5	C_6H_5	0.56
6	Cl	0.66
7	Br	0.67
10	$COOCH_3$	0.87
11	COOH	0.92

A polarographic study of the reduction of three of these compounds was made. No reduction wave was found for unsubstituted 2-chlorophenol or for 4-carboxy-2-chlorophenol. In the case of 4-nitro-2-chlorophenol, reduction waves at about −1.4, −1.7, and −2.1 v. were observed. In view of the results for these three compounds, it appears that the half-wave reduction potentials of the series of 4-substituted 2-chlorophenols lie outside the useful range of the solvent–electrolyte system except in the case of 4-nitro-2-chlorophenol where the *substituent* nitro group is being reduced.

Owing to the inability to measure the reduction half-wave potentials of the 4-substituted 2-chlorophenols, a direct comparison could not be made between the observed frequencies of the spectral transitions and the polarographic oxidation and reduction half-wave potentials as had been planned originally. However, it is still believed that such a comparison for an appropriate series of compounds with a suitable solvent–electrolyte system might lead to theoretically significant conclusions. In this connection, electronic spectral data are already available for 4-substituted[7] and 5-substituted[9] 2-nitrophenols and polarographic reduction and oxidation studies of these two series are in progress.[15]

Experimental

Materials.—The 4-substituted 2-chlorophenols were procured from commercial sources or prepared by methods previously listed in the literature or modifications thereof, as indicated by footnotes in Tables III and IV. The compounds were purified by successive recrystallizations of the solids from appropriate solvents or by distillation of the liquids through a 1 × 40 cm. spinning-band column[16] with a rating of 25 theoretical plates. All water used was deionized by passing distilled water through an Ilco-Way universal deionizing column.[17]

TABLE III

MELTING POINTS OF SOLID 4-SUBSTITUTED 2-CHLOROPHENOLS

4-Substituent	M.p., °C. (cor.)	Lit. m.p., °C.
Cl	40–42	43[a,b]
Br	45.5–46	*a*
COOH	169–171	169–170[a,c]
$COOCH_3$	106–106.5	106–107[d,e]
C_6H_5	75.5–77	76–77.5[a,f]
NO_2	109.5–110.5	111[a,g]
NH_2	149–151 dec.	150–151[h]
$NHCOCH_3$	144.5–145.5	144[h–j]
$N(CH_3)_3^+$	205–206 dec.	*k*

[a] Obtained commercially. [b] "Tables for Identification of Organic Compounds," Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p. 40. [c] E. H. Huntress, "The Preparation, Properties, Chemical Behavior, and Identification of Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 419. [d] Footnote *c*, p. 420. [e] K. von Auwers, *Ber.*, **30**, 1473 (1897). [f] I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, New York, N. Y., 1953, p. 510. [g] Footnote *f*, p. 543. [h] W. G. Christiansen, *J. Am. Chem. Soc.*, **45**, 2193 (1923). [i] J. H. Burckhalter, F. H. Tendick, E. M. Jones, P. A. Jones, W. F. Holcomb, and A. L. Rawlins, *ibid.*, **70**, 1364 (1948). [j] Footnote *f*, p. 461. [k] Prepared by exhaustive methylation of 4-amino-2-chlorophenol with methyl iodide according to the method of R. Pfleger and K. Walmann, *Ber.*, **90**, 2476 (1957). *Anal.* Calcd. for $C_9H_{13}ClINO$: I, 40.47; equiv. wt., 313.6. Found: I, 40.35; equiv. wt., 313.4.

TABLE IV

BOILING POINTS AND REFRACTIVE INDICES OF LIQUID 4-SUBSTITUTED 2-CHLOROPHENOLS

	B.p., °C. (mm.)		$n^{25}D$	
4-Substituent	Exptl.[a]	Lit.	Exptl.	Lit.
H	175–176	175.6[b,c]	1.5571	...
$C(CH_3)_3$	87–88 (2)	234–251[b,d]	1.5302	...
c-C_6H_{11}	128–130 (1)	99–100[b,e] (0.1)	1.5542	1.5527[e]

[a] Corrected. [b] Obtained commercially. [c] Table III, footnote *b*. [d] "Lookin' for Somethin'?," The Dow Chemical Co., Midland, Mich., Jan. 1958; p. 11. [e] Footnote *d*, p. 25.

Ultraviolet Spectra and Measurement of pK_A Values.—The ultraviolet spectra were obtained and the pK_A values were measured as described previously,[7] except that it was necessary to also use a series of Clark and Lubs sodium hydroxide–boric acid stock buffer solutions[18] ranging in pH from 8–10. The results are given in Table I.

The solubility of 4-phenyl-2-chlorophenol in water is exceedingly low and an aqueous solution of optimum concentration could not be prepared. This compound was first dissolved in 10 ml. of 95% ethanol and then made up to volume with deionized water. A reference solution was prepared which contained the same concentration of ethanol. The assumption was made that the small amount (0.5%) of ethanol present would not materially affect the ionization equilibrium.

The visible region of the DK-1 spectrophotometer was checked with a solution of cobaltous chloride prepared by dissolving 2.5382 g. of $CoCl_2 \cdot 6H_2O$ in 1% hydrochloric acid and diluting to 100 ml. with 1% hydrochloric acid. The absorption maximum for cobaltous chloride occurs at 510 mμ. The center of the absorption maximum, as determined experimentally, was measured at 507 mμ which is within experimental error when it is considered that the band is not sharp. The near ultraviolet region was checked by scanning the spectrum of a solution of reagent grade benzene in chromatoquality reagent grade *n*-heptane. Absorption maxima observed at 243, 249, 255, and 261 mμ agree with values previously reported.[19]

Polarographic Reduction of 4-Substituted 2-Chlorophenols at the Dropping Mercury Electrode.—A 0.001 *M* solution (25 ml.) of a 4-substituted 2-chlorophenol in 75% aqueous dioxane[20] was prepared. This solution was also 0.175 *M* in tetrabutylammonium iodide as supporting electrolyte[20] and contained 2 drops of a 0.05% aqueous solution of Triton X-100 (Rohm and Haas) for maximum suppression. The solution was thermostatted for 2 hr. at 25.0 ± 0.1°, purged with dry nitrogen for 30 min. to remove dissolved oxygen, poured into the cathode compartment of a standard three-compartment polarography cell supported in a 25.0 ± 0.1° bath, and the dropping mercury electrode was positioned. Dry nitrogen was passed over the surface of the solution to sweep oxygen from the cell. The anode was a saturated calomel electrode, the center compartment of the cell contained saturated potassium chloride solution, and the compartments were separated by plugs of agar containing potassium chloride. The polarograms were obtained with a Sargent Model XXI polarograph with a polarographic pressure of 45 cm.

This solvent–electrolyte system shows a large wave with a half-wave potential of about −2.4 v. This limiting potential does not appear to be pH dependent since the wave appears at the same place when the system is essentially neutral or brought to pH 11 with aqueous sodium hydroxide or brought to pH 3 with sulfuric acid.

Polarographic Oxidation of 4-Substituted 2-Chlorophenols at the Rotating Platinum Electrode.—A 100-ml. portion of a 0.0001 *M* solution of a 4-substituted 2-chlorophenol in deionized water was prepared. This solution was also 0.14 *M* in lithium chloride as supporitng electrolyte. Other details of apparatus and procedure were the same as above for the polarographic reduction, except one of the outer compartments of the polarography cell was enlarged to accommodate the rotating platinum electrode which was rotated at 600 r.p.m. The results are given in Table II.

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