

The free energy of activation, ΔG^\ddagger , was then calculated from the ΔH^\ddagger and ΔS^\ddagger values at 25° with the usual relationship, $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. The data and calculated values were printed, and a plot was drawn (Figure 3) of $\log (H/kT\tau)$ vs. $1/T$ where T is in degrees Kelvin. The values calculated from a series of measurements including those illustrated in Figure 2 were $\Delta G^\ddagger = 16.4 \pm 0.2$ kcal/mol; $\Delta H^\ddagger = 14.8 \pm 0.2$ kcal/mol; $\Delta S^\ddagger = -5.4 \pm 0.5$ eu. Because of the relatively small separation of lines (3.5 Hz in the low-temperature limit)

and the tendency of the lines to broaden at lower temperatures, we believe more realistic probable limits of error for ΔG^\ddagger and ΔH^\ddagger are ± 2 kcal/mol with a reasonable probability for substantial error in the value of ΔS^\ddagger .

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Relationships between Structure, Polarography, and Electronic Spectra of 4- and 5-Substituted 2-Nitrophenols^{1a}

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Polarographic oxidation potential, $E_{1/2}(\text{OX})$, and reduction potentials, $E_{1/2}(\text{RED})$, for a series of 4- and 5-substituted 2-nitrophenols have been measured in aqueous ethanol (10%) solutions buffered at pH 2.2, 4.0, 6.0, 8.0, and 9.2. Although both series appear to give polarographic waves characteristic of irreversible reactions, good correlations of $E_{1/2}(\text{OX})$ and $E_{1/2}(\text{RED})$ with the appropriate substituent constant, σ_m , σ_p , or σ_p^\ddagger , were obtained. Usually, the correlations that involved $E_{1/2}(\text{RED})$ were most satisfactory at low pH, while those that involved $E_{1/2}(\text{OX})$ were best at high pH. The correlation of the frequency of the longest wavelength maximum observed in the electronic spectrum with $E_{1/2}(\text{OX})$ or $[E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})]$ was examined and found to be good for the 4-substituted compounds and poor for the 5-substituted ones. For the most widely divergent data, an attempt to explain the discrepancies has been made, but the investigation of other series would be desirable.

On the basis of a naive molecular orbital theory, a number of physical properties have been related to the positions of calculated energy levels of organic molecules.² In particular, polarographic oxidation and reduction potentials have been correlated with the calculated energy levels of the ground and first excited states, respectively,^{2a} and the frequencies of certain spectral transitions have been correlated with the differences in energy between these levels.^{2b}

Rather than depending upon the accuracy of such calculations for the correlation of physical and chemical properties, Simpson, Hancock, and Meyers^{3a} measured the electronic spectra of some 4-substituted 2-chlorophenols in acidic and basic aqueous ethanol (5%) and initiated polarographic studies of these materials. However, only oxidation potentials could be obtained in the polarographic work. Similarly, a spectral and polarographic study^{3b} of 4-substituted 2-nitroanilines was attempted but only the spectra and polarographic reduction potentials could be obtained. In this study, two series of compounds, 4- and 5-substituted 2-nitrophenols, have been examined polarographically, since these materials have a known reducible group ($-\text{NO}_2$) and a known oxidizable group ($-\text{OH}$ or $-\text{O}^-$). The electronic spectra of these compounds were obtained previously.^{4,5} It was hoped that a direct comparison of spectral frequencies and the difference between polarographic oxidation and reduction potentials would be possible for substituted 2-nitrophenols and that this

comparison would be independent of the accuracy of any calculations of energy levels. Moreover, Hammett⁶ relations have been used (with varying degrees of success in previous studies^{3,7,8}) for the correlation of spectra and polarographic half-wave potentials with structure, and it was hoped to make more extensive comparisons of these correlations for two series of closely related compounds.

Results and Discussion

The Correlation of Oxidation and Reduction Half-Wave Potentials of 4-Substituted 2-Nitrophenols (I) and 5-Substituted 2-Nitrophenols (II) with Substituent Constants.—The oxidation and reduction half-wave potentials have been measured for the compounds of series I and II at pH 2.2, 4.0, 6.0, 8.0, and 9.2; the results are shown in Tables I and II. Spectral data and σ values for the substituents are shown in Table III.

For both series, calculations of the electron changes, n , from graphs of $E(\text{RED})$ vs. $\log (i_d - i)/i$ did not give integral values for n , where $E(\text{RED})$ is the voltage at a point on a wave front, i_d is the diffusion current, and i is the current at a voltage $E(\text{RED})$. Despite this indication of irreversibility, it was assumed that corresponding electrochemical reactions were obtained in reduction, since each series satisfied certain requirements proposed by Zuman⁹ for the validity of such an assumption. These requirements include a similarity of the wave heights observed which indicates that the same number of electrons are being transferred in the reduction of compounds in the same series, a similarity of the graphs of $E_{1/2}(\text{RED})$ vs. pH, a similarity in the

(1) (a) Abstracted in part from the Ph.D. Dissertation of P. Y. R., Texas A & M University, May 1968. (b) To whom inquiries should be sent.

(2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961: (a) pp 175, 186; (b) p 217.

(3) (a) H. N. Simpson, C. K. Hancock, and E. A. Meyers, *J. Org. Chem.*, **30**, 2678 (1965); (b) J. O. Schreck, C. K. Hancock, and R. M. Hedges, *ibid.*, **30**, 3504 (1965).

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TABLE I
POLAROGRAPHIC OXIDATION AND REDUCTION HALF-WAVE POTENTIALS OF
4-SUBSTITUTED 2-NITROPHENOLS

Compd	4 substituent	$E_{1/2}(\text{RED})^{a,b}$ at pH					$E_{1/2}(\text{OX})^{a,c}$ at pH				
		2.2	4.0	6.0	8.0	9.2	2.2	4.0	6.0	8.0	9.2
1	OCH ₃	0.178	0.272	0.412	0.540	0.723	0.722	0.599	0.461	0.342	0.316
2	CH ₃	0.207	0.300	0.443	0.571	0.745	0.884	0.773	0.612	0.565	0.549
3	H	0.193	0.273	0.422	0.653	0.744	0.999	0.865	0.686	0.603	0.621
4	C ₆ H ₅	0.178	0.303	0.390	0.518	0.683	0.817	0.685	0.541	0.473	0.471
5	Cl	0.127	0.221	0.325	0.500	0.641	0.959	0.834	0.721	0.636	0.680
6	COOCH ₃	0.123	0.230	0.367	0.532	0.648	1.040	0.930	0.832	0.822	0.855
7	COCH ₃	0.142	0.237	0.394	0.576	0.701	1.047	0.916	0.824	0.817	0.847
8	NO ₂	0.082	0.193	0.356	0.492	0.618					

^a Volts vs. saturated calomel electrode. ^b Dropping mercury indicating electrode. ^c Graphite indicating electrode.

TABLE II
POLAROGRAPHIC OXIDATION AND REDUCTION HALF-WAVE POTENTIALS OF
5-SUBSTITUTED 2-NITROPHENOLS

Compd	5 substituent	$E_{1/2}(\text{RED})^{a,b}$ at pH					$E_{1/2}(\text{OX})^{a,c}$ at pH				
		2.2	4.0	6.0	8.0	9.2	2.2	4.0	6.0	8.0	9.2
9	OCH ₃	0.283	0.375	0.518	0.647	0.825	1.039	0.906	0.748	0.648	0.655
10	CH ₃	0.222	0.318	0.436	0.594	0.767	0.978	0.844	0.676	0.578	0.562
11	CH ₃ CONH	0.239	0.318	0.447	0.585	0.717	1.010	0.876	0.702	0.611	0.592
12	H	0.193	0.237	0.422	0.653	0.744	0.999	0.865	0.686	0.603	0.621
13	Cl	0.144	0.242	0.371	0.532	0.684	1.026	0.900	0.760	0.720	0.742
14	COOCH ₃	0.092	0.176	0.292	0.442	0.605	1.016	0.871	0.726	0.687	0.682
15	NO ₂	0.042	0.125	0.246	0.355	0.445	1.085	0.948	0.861	0.865	0.885
16	CHO	0.070	0.152	0.262	0.412	0.622	1.027	0.874	0.744	0.716	0.742

^a Volts vs. saturated calomel electrode. ^b Dropping mercury indicating electrode. ^c Graphite indicating electrode.

TABLE III
SUBSTITUENT CONSTANTS AND ELECTRONIC SPECTRAL DATA FOR 4- AND 5-SUBSTITUTED 2-NITROPHENOLS

Compd	Substituent	σ_m^c	σ_p^c	$\sigma_p^{\pm d}$	4 substituent ^a		5 substituent ^b	
					ν_B^e	ν_A^f	ν_B^e	ν_A^f
1	OCH ₃	0.115	-0.268	-0.778	21,978	25,575	24,510	28,980
2	CH ₃	-0.069	-0.170	-0.311	23,095	27,174	23,810	28,730
3	H	0.000	0.000	0.000	24,155	28,571	23,920	28,570
4	CH ₃ CONH	0.248	-0.015	-0.600	23,310	26,667	24,210	28,330
5	C ₆ H ₅	0.060	-0.010	-0.179	22,727	26,455	23,700	30,580
6	Cl	0.373	0.227	0.114	23,474	27,624	24,420	29,240
7	COOCH ₃	0.315	0.385 ^g	0.636	25,000	29,326	23,470	28,090
8	COCH ₃	0.376	0.502	0.874	25,126	29,412	22,930	27,850
9	NO ₂	0.710	0.778	1.270			22,620	27,510
10	CHO	0.382	0.425 ^h	1.126			22,930	27,850

^a Reference 4. ^b Reference 5. ^c Reference 10. ^d Reference 11. ^e ν_B in $\text{cm}^{-1} = 1/\lambda_{\text{max}}^{\text{NaOH}} \times 10^7$ for the longest wavelength. ^f ν_A in $\text{cm}^{-1} = 1/\lambda_{\text{max}}^{\text{HCl}} \times 10^7$ for the longest wavelength. ^g H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim. Pays-Bas*, **78**, 815 (1959). ^h M. Charton, *J. Org. Chem.*, **28**, 3121 (1963); A. A. Humfray, J. J. Ryan, J. P. Warren, and Y. H. Yung, *Chem. Commun.*, 610 (1965).

character of the limiting currents, and a similarity in the degree of reversibility. Only 3-hydroxy-4-nitrobenzaldehyde (the 5-CHO compound of series II) was found to give a reduction diffusion current different from the others, and it was thought best to exclude it from the regression analysis of $E_{1/2}(\text{RED})$ vs. σ_p^{10} or $\sigma_p^{\pm 11}$. The 2,4- and 2,5-dinitrophenols each showed two distinct reduction waves for the two nitro groups. In both cases, the first of the two waves was used for the various correlations described below.

For both series I and II, the magnitude of the potential required for reduction increases with increasing pH (Tables I and II). The plots of reduction half-wave potentials vs. substituent constants (Figures 1-3) have positive slopes indicating that substituents which increase the electron density increase the magnitude of the potential required for reduction. This is to be

expected since any factor which increases the electron density at the site of the reduction would make it more difficult to add electrons.

As shown by entries 1-5 in Table IV, the correlation between $E_{1/2}(\text{RED})$ and σ_m^{10} for series I is poor at pH 6.0 and 8.0, good at pH 9.2, and excellent at pH 2.2 (Figure 1) and 4.0. The precision obtainable for the polarographic reduction potential, based upon the present study, is approximately ± 0.005 V and the uncertainty in σ_m is approximately ± 0.01 , so that the estimated standard deviations agree fairly well with the values of s at pH 2.2 and 4.0.

As shown by entries 16-20 in Table V, the correlation between $E_{1/2}(\text{RED})$ and σ_p for series II is good at pH 8.0, slightly better at pH 2.2 (Figure 2), 4.0, and 6.0, and excellent at pH 9.2. The least significant correlations between $E_{1/2}(\text{RED})$ and σ for both series I and II occur at pH 6.0 and 8.0. Entries 21-25 for series II in Table V show that at low pH there are better correla-

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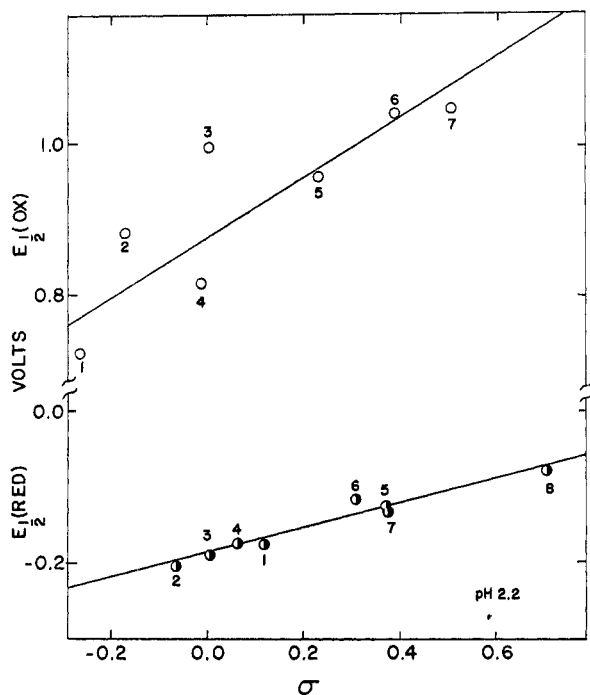


Figure 1.—The relationship between $E_{1/2}(\text{RED})$ and σ_m (●) and between $E_{1/2}(\text{OX})$ and σ_p (○) for 4-substituted 2-nitrophenols (I). Numbers refer to compounds as listed in Table I.

TABLE IV
REGRESSION ANALYSIS DATA FOR $E_{1/2}$ vs. σ
FOR 4-SUBSTITUTED 2-NITROPHENOLS (I)

Entry	pH	$E_{1/2}^b$	ρ^c	r^d	s^e	% confidence level ^f
$E_{1/2}(\text{RED}) = E_{1/2}^0(\text{RED}) + \rho\sigma_m, n = 8^a$						
1	2.2	-0.192	0.160	0.984	0.008	>99.95
2	4.0	-0.288	0.145	0.944	0.014	>99.95
3	6.0	-0.415	0.114	0.765	0.027	97.3
4	8.0	-0.576	0.121	0.597	0.045	88.2
5	9.2	-0.726	0.162	0.856	0.027	99.3
$E_{1/2}(\text{OX}) = E_{1/2}^0(\text{OX}) + \rho\sigma_p, n = 7^a$						
6	2.2	0.890	0.360	0.844	0.072	98.3
7	4.0	0.766	0.359	0.836	0.074	98.1
8	6.0	0.625	0.449	0.920	0.060	99.7
9	8.0	0.555	0.559	0.919	0.075	99.7
10	9.2	0.559	0.640	0.934	0.077	99.8
$E_{1/2}(\text{OX}) = E_{1/2}^0(\text{OX}) + \rho\sigma_p^\pm, n = 7^a$						
11	2.2	0.914	0.197	0.909	0.056	99.5
12	4.0	0.790	0.196	0.903	0.058	99.5
13	6.0	0.656	0.236	0.953	0.046	99.9
14	8.0	0.593	0.298	0.966	0.049	>99.95
15	9.2	0.603	0.337	0.969	0.053	>99.95

^a Number of experimental points used. ^b Regression intercept. ^c Regression slope. ^d Linear correlation coefficient. ^e Standard deviation from regression. ^f Based on Student's *t* test (ref 13).

tions between $E_{1/2}(\text{RED})$ and exalted substituent constants, σ_p^\pm , which indicates that for this series resonance effects may be of substantial importance (Figure 3). Moreover, the values of *s* obtained at pH 2.2 and 4.0 are in fair agreement with those expected from the experimental errors thought to be present and are similar to the results for series I.

The effect of pH upon the reduction of the compounds involved is complicated, but the good correlations obtained at low pH appear to accompany the small, nearly parallel variation of $E_{1/2}(\text{RED})$ with pH for pH 2.2 and 4.0.⁹

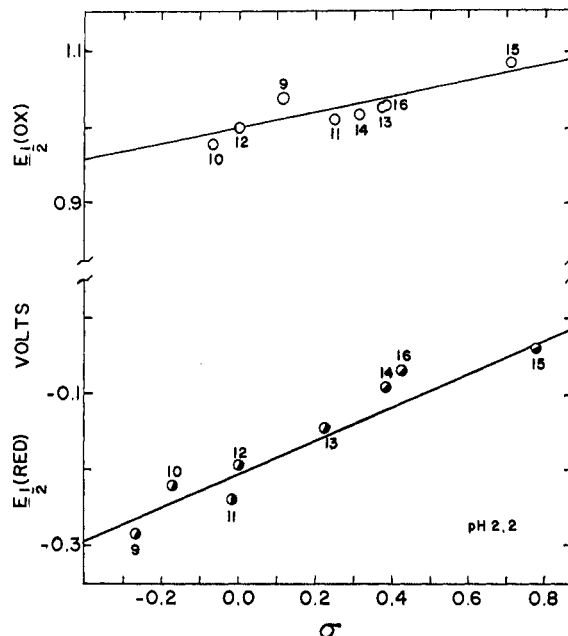


Figure 2.—Relationships between $E_{1/2}(\text{RED})$ and σ_p (●) and between $E_{1/2}(\text{OX})$ and σ_m (○) for 5-substituted 2-nitrophenols (II). Numbers refer to compounds as listed in Table II.

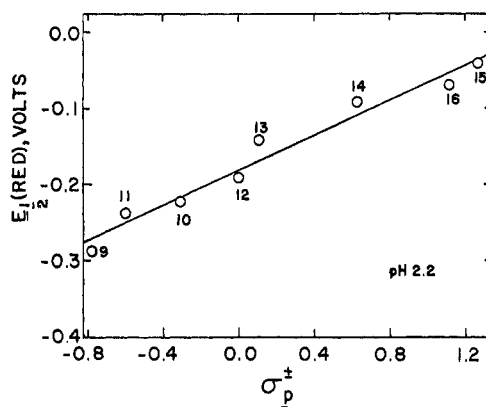


Figure 3.—The relationship between $E_{1/2}(\text{RED})$ and σ_p^\pm for 5-substituted 2-nitrophenols (II). Numbers refer to compounds as listed in Table II.

The polarographic oxidation of the compounds of both series can probably best be described as the oxidation of the $-\text{OH}$ or $-\text{O}^-$ group by loss of electrons from the molecule as the first step.⁹ Plots of $E_{1/2}(\text{OX})$ vs. $\log(i_d - i)/i$ revealed that these reactions are irreversible. It was assumed, however, that corresponding electrochemical reactions are taking place in all cases since these oxidation reactions, like the reductions, follow Zuman's⁹ criteria for the validity of such assumptions. The magnitude of the potential required for oxidation decreases with increasing pH (Tables I and II), and substituents which decrease the electron density on the hydroxyl group increase the potential required for oxidation while those which increase the electron density lower the potential required for oxidation (Figures 1, 2, and 4).

The effect of pH upon oxidation is complicated, but the good correlations obtained at high pH appear to accompany the small variation of $E_{1/2}(\text{OX})$ with pH for pH 8.0 and 9.2.⁹ Also, the poor correlations at the more acidic pH 2.2 and 4.0 may be partly due to the

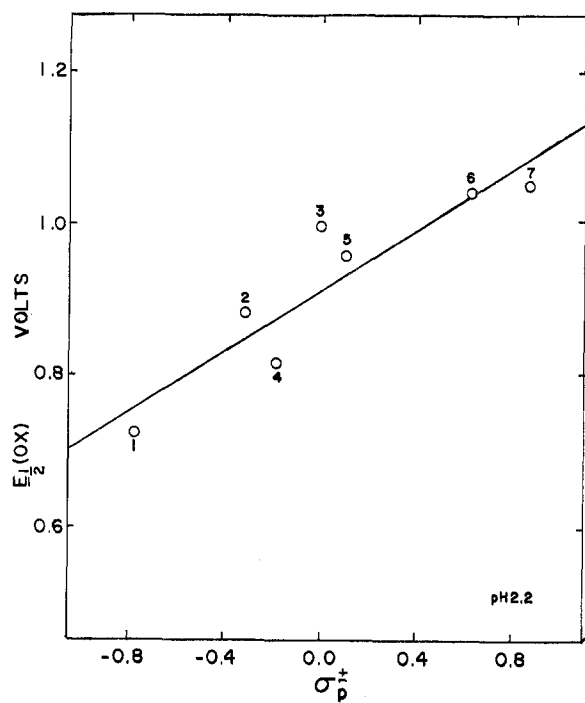


Figure 4.—Relationship between $E_{1/2}(\text{OX})$ and σ_p^+ for 4-substituted 2-nitrophenols (I). Numbers refer to compounds as listed in Table I.

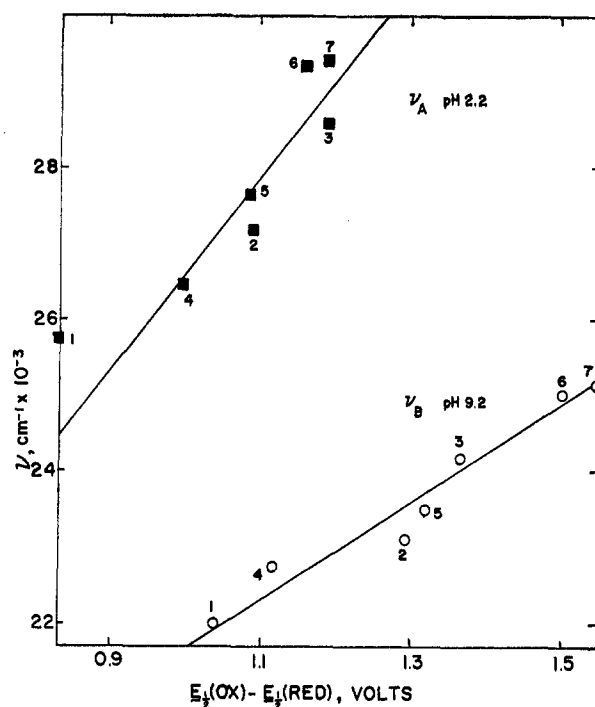


Figure 5.—The relationship between ν_A and $[E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})]$ (■) and between ν_B and $[E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})]$ (○). Numbers refer to compounds as listed in Table I.

TABLE V
REGRESSION ANALYSIS DATA FOR $E_{1/2}$ vs. σ
FOR 5-SUBSTITUTED 2-NITROPHENOLS (II)

Entry	pH	E^b	ρ^c	r^d	s^e	% confidence level ^f
$E_{1/2}(\text{RED}) = E_{1/2}^0(\text{RED}) + \rho\sigma_p, n = 7^a$						
16	2.2	-0.204	0.229	0.968	0.023	>99.95
17	4.0	-0.293	0.236	0.974	0.022	>99.95
18	6.0	-0.424	0.253	0.966	0.027	>99.95
19	8.0	-0.583	0.289	0.946	0.039	99.9
20	9.2	-0.730	0.344	0.987	0.022	>99.95
$E_{1/2}(\text{RED}) = E_{1/2}^0(\text{RED}) + \rho\sigma_p^+, n = 7^a$						
21	2.2	-0.179	0.118	0.985	0.016	>99.95
22	4.0	-0.267	0.120	0.985	0.016	>99.95
23	6.0	-0.396	0.129	0.975	0.023	>99.95
24	8.0	-0.551	0.139	0.900	0.053	99.4
25	9.2	-0.692	0.165	0.942	0.046	99.9
$E_{1/2}(\text{OX}) = E_{1/2}^0(\text{OX}) + \rho\sigma_m, n = 8^a$						
26	2.2	0.997	0.103	0.856	0.017	99.3
27	4.0	0.859	0.102	0.790	0.021	98.0
28	6.0	0.683	0.211	0.899	0.028	99.8
29	8.0	0.587	0.352	0.949	0.031	>99.95
30	9.2	0.585	0.385	0.921	0.044	99.9

^a Number of experimental points used. ^b Regression intercept. ^c Regression slope. ^d Linear correlation coefficient. ^e Standard deviation from regression. ^f Based on Student's *t* test (ref 13).

difficulty in measuring the half-wave potentials, since at these pH's the limiting current of the polarographic waves is very near the decomposition potential of the solvent. For series I, there is a better correlation between $E_{1/2}(\text{OX})$ and σ_p^+ (Table IV, entries 11–15) than between $E_{1/2}(\text{OX})$ and σ_p (Table IV, entries 6–10), indicating that resonance effects are important (Table IV, Figures 1 and 4). The oxidation potentials are reproducible to within ± 0.015 V.

It can be generally concluded that good correlations exist between $E_{1/2}$ and σ for series I and II and that

these correlations will fairly well predict new $E_{1/2}$ values from known σ values for other members of series I and II. The results show that the predictions for $E_{1/2}(\text{RED})$ are likely to be more reliable than those for $E_{1/2}(\text{OX})$ and that the uncertainty in the predicted values depends appreciably upon pH.

Correlation of Polarographic Oxidation and Reduction Half-Wave Potentials with Electronic Spectra.—If the polarographic oxidation and reduction half-wave potentials are linearly related to the ground and first excited states, respectively, then the difference $[E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})]$ should be proportional to the energy required to raise an electron from the ground state to the first excited state, and it was hoped that a good correlation could be found between $[E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})]$ and the frequency of the longest wavelength electronic absorption maximum.

For series I, there are good correlations between the acidic and basic electronic absorption frequencies,⁴ ν_A and ν_B , and the difference in the oxidation and reduction potentials at the five pH's as shown in entries 31–35 of Table VI and in Figure 5. The standard deviations in entries 33–35 in Table VI are better than would be expected from the uncertainties in the measurements of the absorption frequencies (442 cm^{-1} acidic, 367 cm^{-1} basic) and the uncertainties in the measurements of the oxidation and reduction half-wave potentials.

The effect of substituents on the energies of the ground and excited states can be seen in Figure 1 where both oxidation and reduction half-wave potentials have been plotted on the same graph vs. the normal σ values. It is evident from Figure 1 that the difference in the energies of the ground and excited states increases with an increase in electron withdrawal. Also the ground-state energy seems to be affected to a greater degree by electron withdrawal than the excited state.

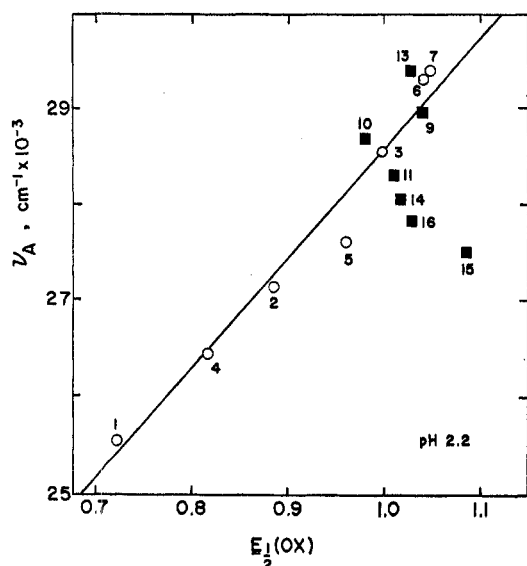


Figure 6.—Relationship between ν_A and $E_{1/2}(\text{OX})$ for 4-substituted 2-nitrophenols (○) and 5-substituted 2-nitrophenols (■). Numbers refer to compounds as listed in Tables I and II.

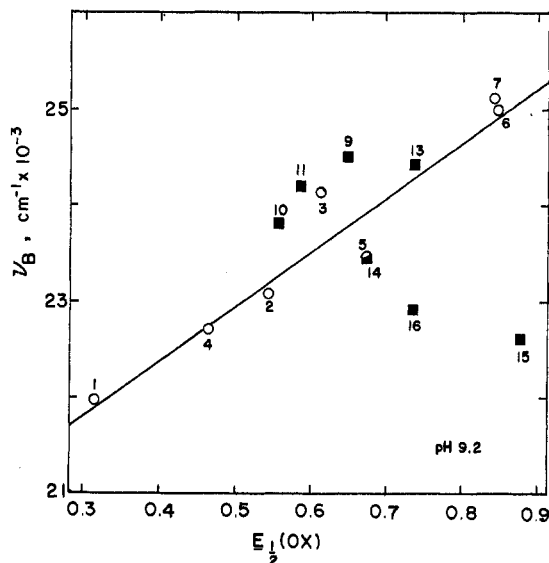


Figure 7.—Relationship between ν_B and $E_{1/2}(\text{OX})$ for 4-substituted 2-nitrophenols (○) and for 5-substituted 2-nitrophenols (■). Numbers refer to compounds as listed in Tables I and II.

TABLE VI
REGRESSION ANALYSIS DATA FOR ν vs.
[$E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})$] AND ν vs.
[$E_{1/2}(\text{OX})$] FOR 4-SUBSTITUTED 2-NITROPHENOLS (I)

Entry	pH	ν	ν^0 ^b	C ^c	r ^d	s ^e	% confidence level ^f
$\nu = \nu^0 + C[E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})], n = 7^a$							
31	2.2	ν_A	13,903	12,703	0.954	479	99.9
32	4.0	ν_A	13,617	13,284	0.957	461	99.9
33	6.0	ν_A	15,872	11,174	0.985	278	>99.95
34	8.0	ν_B	16,417	6,214	0.987	205	>99.95
35	9.2	ν_B	15,232	6,388	0.982	243	>99.95
$\nu = \nu^0 + C[E_{1/2}(\text{OX})], n = 7^a$							
36	2.2	ν_A	16,916	11,707	0.983	295	>99.95
37	4.0	ν_A	18,421	11,637	0.981	307	>99.95
38	6.0	ν_A	21,006	10,069	0.965	416	>99.95
39	8.0	ν_B	19,677	6,532	0.968	320	>99.95
40	9.2	ν_B	20,073	5,771	0.964	341	>99.95

^a Number of experimental points used. ^b Regression intercept. ^c Regression slope. ^d Linear correlation coefficient. ^e Standard deviation from regression. ^f Based on Student's *t* test (ref 13).

This finding is in accord with the theoretical discussion of Matsen¹² for monosubstituted benzenes.

The correlation of ν_A or ν_B with $E_{1/2}(\text{RED})$ or $E_{1/2}(\text{OX})$ alone for series I is rather surprising. The correlations¹³ with $E_{1/2}(\text{RED})$ are not significant, but those with $E_{1/2}(\text{OX})$ are good as shown by entries 36–40 in Table VI and by Figures 6 and 7 at pH 2.2 and 9.2. The regression lines drawn in Figures 6 and 7 are for entries 36 and 40 of Table VI and apply only to the seven members of series I (open circles). The shaded squares in these figures apply to members of series II and are plotted only for ready comparison.

Thus, for series I, it appears that the correlations of ν_A with $E_{1/2}(\text{OX})$ alone at low pH are actually superior to those of ν_A with [$E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})$].

For series II, there are no significant correlations between $E_{1/2}(\text{OX})$, $E_{1/2}(\text{RED})$, or [$E_{1/2}(\text{OX}) -$

$E_{1/2}(\text{RED})$] and absorption frequencies, with or without the inclusion of the 5-NO₂ and 5-CHO compounds. The graphical display of ν_A and ν_B vs. [$E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})$] at pH 2.2 and 9.2, respectively, for all data for I and II, are given in Figures 8 and 9. The regression lines shown are for the data of I only. The data for II appear to scatter around the regression lines calculated for I, and it seems clear that some important effects are unaccounted for in II compared to I. There are four points that deviate greatly from the regression lines shown. These are for substituents 5-OCH₃ and 5-CH₃CONH in acid solution, and 5-CHO and 5-NO₂ in basic solutions. An examination of the spectral results available⁵ shows that the extinction coefficients for the 5-OCH₃ and 5-CH₃CONH compounds are anomalously large in acid solution, which may indicate that these compounds do not belong to the same spectral series as the others. As mentioned above, the diffusion current for the 5-CHO compound in reduction differs from that of any of the others obtained, and there is perhaps an ambiguity in the reduction process for the 5-NO₂ compound, but the very large deviations observed in basic solutions are not present in acid solution. Moreover, the deviations appear to be in the wrong direction if the reduction processes in these materials occur at $E_{1/2}(\text{RED})$ values that are smaller in magnitude than expected from the appropriate regression analyses.

In the graphs of ν vs. $E_{1/2}(\text{OX})$ (Figures 6 and 7, dark squares) for series II the most widely divergent points are the 5-CHO and 5-NO₂ compounds. These are the same points which deviate the most in the graphs of ν vs. [$E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})$]. These deviations cannot be explained since there is no reason to suspect that the oxidations or the spectra for these compounds are anomalous.

Thus, the correlations of spectral frequencies ν_A and ν_B with the appropriate values of [$E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})$] or $E_{1/2}(\text{OX})$ alone appear to be satisfactory for series I, but not for series II, and further studies on other series of compounds are needed in order to in-

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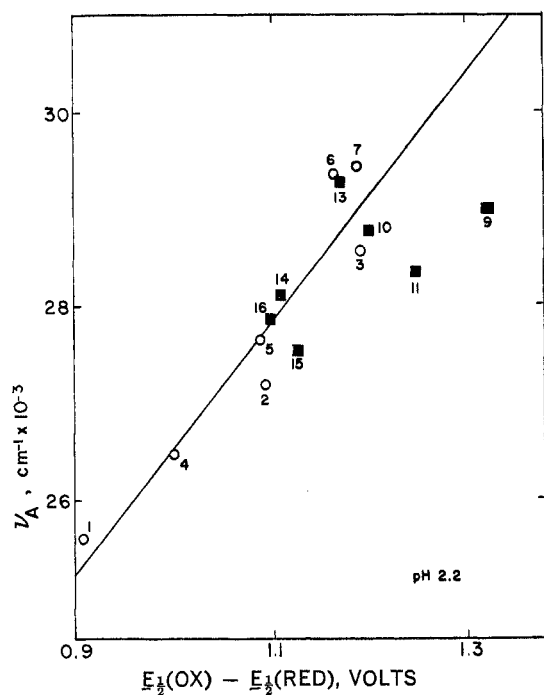


Figure 8.—Relationship between ν_A and $[E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})]$ for 4-substituted 2-nitrophenols (O) and for 5-substituted 2-nitrophenols (■). Numbers refer to compounds as listed in Tables I and II.

investigate these internal correlations of different measured properties of similar molecules.

Experimental Section

Materials.—The 4- and 5-substituted 2-nitrophenols used in this study were prepared and purified as reported previously.^{4,5}

USP reagent quality absolute ethanol was used. Aqueous MacIlvane buffer solutions¹⁴ (pH 2.2, 4.0, 6.0, 8.0) were prepared from reagent grade materials and water which had been deionized by passage through an Ilco Way universal deionizing column.¹⁵ An aqueous Clark and Lub¹⁴ buffer (pH 9.2) was prepared from deionized water and reagent grade boric acid and sodium hydroxide.

Commercially available spectrographic quality graphite rods¹⁶ (1/8-in. diameter) were used as indicating electrodes for measuring the oxidation potentials.

Deionized water, triply distilled mercury, and reagent grade mercurous chloride and potassium chloride were used to prepare the saturated calomel reference electrode¹⁷ (see). Triply distilled mercury was also used in the dropping mercury indicating electrode (dme).

Measurement of Polarographic Half-Wave Potentials.—A 0.00025 *M* solution in buffered 10 vol % aqueous ethanol of a substituted 2-nitrophenol was prepared by dilution of 5 ml of a 0.0025 *M* solution in absolute ethanol to 50 ml with the appropriate buffer. (Owing to low solubility of 4-phenyl-2-nitrophenol, the 0.00025 *M* solution was prepared in buffered 30 vol % aqueous ethanol.) A 25-ml portion of solution (25°) and 6 drops of maximum suppressor (2 vol % aqueous Triton X-100) were placed in the appropriate compartment of an H-type cell with an sce in the other compartment. The solution (25°) was purged for 10 min with dry nitrogen saturated with vapor from 10 vol % aqueous ethanol and the polarographic half-wave potential was measured with a Metrohm Polarecord Model E 261 polarograph.

For the polarographic reduction half-wave potentials, the dme, as indicating electrode, was placed in the test solution with

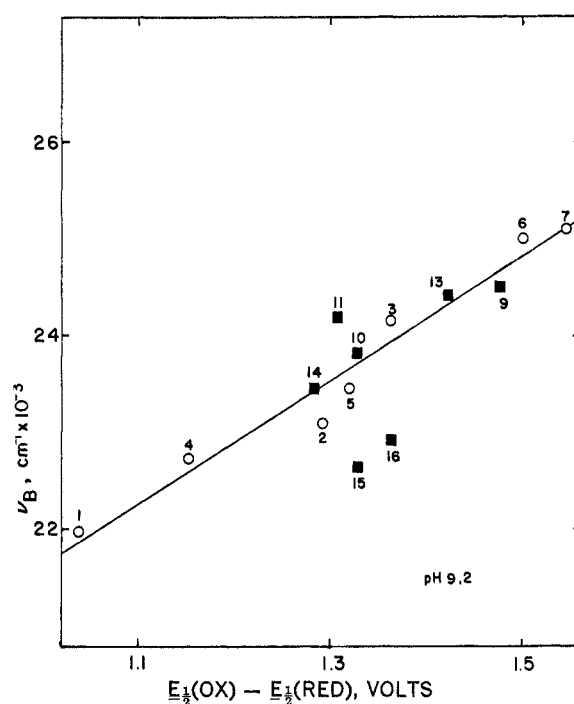


Figure 9.—Relationship between ν_B and $[E_{1/2}(\text{OX}) - E_{1/2}(\text{RED})]$ for 4-substituted 2-nitrophenols (O) and for 5-substituted 2-nitrophenols (■). Numbers refer to compounds as listed in Tables I and II.

the capillary tip 0.25 in. beneath the surface, and the potentials were measured at a pressure of 52 cm with a drop time of 3.2 sec. For the system studied, the dme has a usable range (pH dependent) to -2.1 V.

For the polarographic oxidation half-wave potential, a sharpened graphite electrode¹⁸ was used as the indicating electrode. This electrode was inserted through a one-hole rubber stopper and placed so that the tip extended 1/8 in. below the surface of the solution. It was necessary to renew the tip of the electrode after each run since, unless this was done, the wave heights decreased in successive runs of the same solution. (This effect was probably caused by contamination of the electrode surface.) Other details of the solution, apparatus, and procedure were the same as above for the polarographic reduction. For the system studied, the graphite electrode has a usable range to $+1.1$ V.

The half-wave potentials were determined by the point method.¹⁹ The polarograms were of the standard "S" shape and no maxima were observed.

The diffusion currents, which are dependent on concentration and electrode surface area, could be accurately measured and reproduced for the reduction waves. However, for the oxidation waves, the surface area of the electrode varied from run to run, and therefore the diffusion currents also varied.

Reduction half-wave potentials were reproducible to ± 0.005 V while the oxidation half-wave potentials were reproducible to ± 0.015 V. The polarograph was checked for accuracy by determining the reduction half-wave potential of Pb^{2+} (0.005 *M* lead nitrate) in 0.1 *M* aqueous potassium chloride solution. The value of 0.396 V obtained agrees satisfactorily with that of 0.40 V reported previously.

Registry No.—Table I—1, 1568-70-3; 2, 119-33-5; 3, 88-75-5; 4, 885-82-5; 5, 89-64-5; 6, 99-42-3; 7, 6322-56-1; 8, 51-28-5; Table II—9, 704-14-3; 10, 700-38-9; 11, 712-34-5; 13, 611-07-4; 14, 713-52-0; 15, 329-71-5; 16, 704-13-2.

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The Spontaneous Hydrolysis of Sulfonyl Fluorides¹

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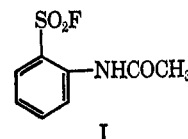
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The rates of spontaneous hydrolyses of substituted benzenesulfonyl fluorides in dioxane-water (40:60 v/v) at 45.0 or 65.5° follow the sequence $o\text{-CH}_3\text{CONH} > p\text{-NO}_2 > m\text{-NO}_2 > o\text{-NO}_2 > p\text{-Br} > m\text{-CH}_3\text{CONH} > \text{H}$. The hydrolyses were too slow to be followed when the substituent was $p\text{-CH}_3\text{O}$, $o\text{-NH}_2$, $p\text{-NH}_2$, or $p\text{-CH}_2\text{CONH}$. The substituent effects are generally very similar to, but larger than, those found for sulfonyl chlorides and $\rho \cong 1.8$. The relatively rapid hydrolysis of o -acetamidobenzene sulfonyl fluoride is accompanied by loss of the acetyl group, suggesting that a neighboring-group participation of the acetamido group gives an unstable intermediate.

Sulfonyl fluorides are generally unreactive toward acidic and neutral water and hydroxylic solvents;³⁻⁵ for example, Swain and Scott showed that benzenesulfonyl fluoride was much less reactive (by a factor of $ca. 5 \times 10^3$) than the corresponding chloride, although it reacted readily with hydroxide ion.⁵ The results were explained in terms of the strong S-F bond and the strong electron withdrawal by fluorine. However, azo dyes derived from p -aminobenzenesulfonyl fluoride react readily with cellulose, cellulose acetate, and some synthetic fibers.⁶ In addition, Baker and his coworkers have shown that some sulfonyl fluorides are very effective enzyme inhibitors, and that the sulfonyl group is bound irreversibly near to the active site.⁷ Moreover enzymes catalyzed the hydrolysis of some sulfonyl fluorides,⁸ and Baker suggested that these nucleophilic attacks upon sulfonyl fluorides occur with assistance from a hydrogen-bonding donor which assists S-F bond breaking. This hydrogen-bonding donor could be an external water molecule or a protic group in the enzyme, and the nucleophile could be a group in the enzyme or an external water molecule. The fact that the hydrolysis of acyl fluorides, but not chlorides, is acid catalyzed⁹ suggests that a general acid or a proton assists departure of the fluoride but not the chloride ion in water.

The aim of the present work was to examine structural effects upon the rate of the spontaneous hydrolysis of arylsulfonyl fluorides because the solvolyses of the corresponding chlorides have been studied in great detail, and all the evidence points to nucleophilic attack in the rate-limiting step although there is question as to the relative importance of bond making and breaking.¹⁰⁻¹³ The unreactivity of the arylsulfonyl fluorides

prevented our studying, quantitatively, compounds containing electron-donating groups. In addition we examined the hydrolysis of o -acetamidobenzenesulfonyl fluoride (I), because a derivative of this compound has been found to be surprisingly reactive to water whereas compounds derived from m -acetamidobenzenesulfonyl fluoride showed no such reactivity.¹⁴



Experimental Section

Materials.—The following sulfonyl fluorides were obtained commercially and were recrystallized from ethanol-water: o -aminobenzene (Aldrich), mp 62–64° (lit.¹⁵ 64–65°); p -aminobenzene (Aldrich), mp 70–71° (lit.¹⁵ 70°); p -acetamidobenzene (Aldrich), mp 175–177° (lit.¹⁵ 174–176°); m -nitrobenzene (Alfred Bader), mp 46–47° (lit.¹⁵ 46–48°). The other sulfonyl fluorides were prepared by refluxing the chlorides with KF in aqueous dioxane for 0.5–1 hr or by acylating the aminosulfonyl fluoride.^{3,14} The reaction solution was poured into cold water, the liquid sulfonyl fluorides were extracted, usually into ether, the organic layer was washed with water and then dried, and the fluoride was distilled *in vacuo*. The solid fluorides were removed by filtration and recrystallized from methanol-water, ethanol-water, or benzene. The sulfonyl fluorides prepared from the chloride with fluoride ion had the following physical properties: benzenesulfonyl fluoride, bp 60–61° (1.5 mm) [lit.⁵ 83° (3 mm)]; o -nitro-, mp 52–54° (lit.¹⁵ 55–58°); p -nitro-, mp 75–78° (lit.¹¹ 77–79°); p -methoxy-, bp 103–105° (1.7 mm) [lit.¹⁶ 175° (60 mm)]; p -bromo-, mp 65–66° (lit.¹⁷ 65–66°). The infrared spectrum of the p -bromo compound was very similar to that in the literature.¹⁸ o - and m -acetamidobenzenesulfonyl fluorides were

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