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Electrochemical Reductions of the Chlorinated Nitrobenzenes: A $\rho\Sigma\sigma^\circ$ Correlation with Corrections for Adjacent Chlorine Interactions†

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The first electrochemical reductions for all the chlorinated nitrobenzenes, except the pentachloro, at a mercury-coated platinum cathode in Me$_2$SO are reversible one-electron processes. A $\rho\Sigma\sigma$ correlation of the peak potentials show that the σ constants are nonadditive. However, additivity was obtained by applying an empirically determined correction factor (σ_α) for adjacent chlorine pairs. Normal σ constants (σ°) rather than the usual primary σ constants were required for the best data fit. This is consistent with the formation of a radical anion in which the chlorine is non- or anti-π-bonding. The quality of the $\rho\Sigma\sigma$ correlation was further improved by separating the correction term into σ_α(om) and σ_α(mp) which are functions of the adjacent σ constants. This also allowed an independent approximation of $\sigma_o{}^\circ$ constant for chlorine. The steric effects of both one and two ortho chlorines were determined and show that within experimental error $\rho_{m,p} = \rho_o = \rho_{o,o}$, while the steric offsets $\Delta E_s(o)$ and $\Delta E_s(o,o)$ are much larger than those previously estimated for this reaction. There was no evidence of a steric "buttressing" effect by meta chlorines on the ortho chlorines.

Introduction

During our investigations of factors controlling the anaerobic degradation of pesticides and other xenobiotic compounds,[1] we have had the opportunity to obtain cyclic voltammetry data on the reduction of nitrobenzene and all 19 of its chlorinated analogues in dimethyl sulfoxide (Me$_2$SO). The high quality of these data has permitted a detailed analysis of the effects of multiple chlorine substituents in Hammett-type linear free-energy correlations. In the Hammett $\sigma\rho$ treatment it is generally accepted that the effect of multiple substituents on a reaction center is additive with respect to their substituent constants (σ_x). This additivity has been shown for substituents on the same ring,[2] as well as on separate rings attached to the same reaction center.[3] However, in the aliphatic series, using Taft's σ^* values, multiple chlorine substituents are an example where the constants are not additive. Compared to the value for CH$_2$Cl, the σ^* values are 3.8% and 5.3% low per chlorine for CHCl$_2$ and CCl$_3$, respectively.[4] Nonadditivity of substituent constants is often taken as a sign of (1) a change in the reaction mechanism,[5] (2) a steric effect on the reaction center,[6] (3) specific ortho interactions, such as field effects and steric and resonance interactions,[7] or (4) major changes in solvation.[8] Shorter[9] notes that "additivity is less strict when the electronic effect is large, as in -CHCl$_2$ or -CCl$_3$", but he gives no explanation for the cause of nonadditivity.

The first electrochemical reduction wave of nitrobenzenes has been used for linear free-energy analysis of substituent effects,[10] mainly by $\sigma\rho$ treatment.[11] Literature data for half-wave potentials (E_h) of a wide range of substituted nitrobenzenes in protic solvents have been analyzed by Zuman[11c] using σ and σ^- constants. Under these conditions the reductions were irreversible and pH dependent, leading to ρ values which were quite variable. In the aprotic solvents acetonitrile and dimethylformamide, the first reduction wave of nitrobenzenese is reversible and produces the "stable" radical anion. More consistent ρ values were obtained under these conditions, but the range of substituents was limited mainly to halogens and alkyl groups.[11ab] Ordinary Hammett σ constants were used in these analyses and neither correlation coefficients nor standard deviations were given to assess the quality of the correlation.

In the aprotic solvents a steric offset in the reduction potential (ΔE_s) of about −60 mV for an ortho chlorine or methyl group and of −180 mV for two ortho chlorines or methyl groups was determined, based on the assumption that σ_o and σ_p are equal.[11ab] In protic solvents little if any steric effect is reported,[11c] perhaps reflecting the irreversible nature of the reductions. An appreciable steric effect is expected, as spectral and X-ray data[12] show that in the neutral molecule the nitro group is twisted about 30–40° with one ortho substituent (methyl or chlorine) and about 65° for two. From calculations based on electron-spin densities, the twist is about the same in the radical anions with ortho methyls. An anomalously large steric effect on −110 mV has been noted[13] for 2,3-dichloronitrobenzene and ascribed to "buttressing" of the ortho chlorine by the meta chlorine, causing a greater twist in the nitro group. No buttressing effect was apparent in the methyl-substituted series.[10b]

In this paper we analyze the cause of deviation from, and the corrections needed for, additivity of σ constants for multiple chlorine substituents in a $\sigma\rho$ correlation. We also find which class of σ constants are appropriate for the

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† Contribution No. 1242.

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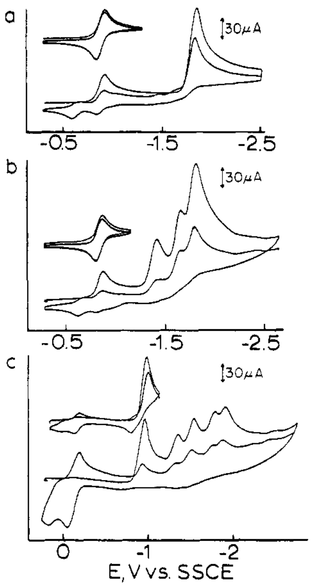

Figure 1. Typical voltammograms showing reversible nature of first wave except for pentachloronitrobenzene. Conditions are 0.5 mM substrate in Me_2SO with 0.1 M TEAP and a sweep rate of 75 mV/s with a saturated aqueous Ag|AgCl reference electrode: (a) 3-chloronitrobenzene, (b) 2,3,4-trichloronitrobenzene, and (c) pentachloronitrobenzene. Note, the reversible oxidation seen near 0 V in c on the return sweep is due to mercury oxidation when chloride ion is produced during reduction of the substrates. This indicates that pentachloronitrobenzene loses chloride on the first reduction step.

electrochemical reduction of chlorinated nitrobenzenes. For compounds with one and two ortho chlorines we determine the magnitude of their steric effect and test the independence of ρ.

Results

Cyclic Voltammetry Data. Cyclic voltammograms of nitrobenzene and all of the chlorinated analogues were obtained in Me_2SO solutions containing 0.1 M tetraethylammonium perchlorate (TEAP) at a mercury-coated platinum flag electrode with a sweep rate of 75 mV/s. Some typical voltammograms are shown in Figure 1. Except for pentachloronitrobenzene, the first reduction waves were reversible as shown by superimposable multiple cycles around the first wave and equal magnitudes for cathodic and anodic currents. Also the reductive and oxidative peak potentials (E_p) were separated by about 60 mV, which is typical for a reversible one-electron reduction forming the anion radical.[14] Subsequent reduction processes at more negative potentials are irreversible and their analyses will be treated in a later paper.

The first reduction wave of the pentachloro compound is a multiple-electron irreversible process, apparently due to the merging of a subsequent irreversible reduction with the initial reversible process. We have included this E_p value in our correlations as it fits the data sets and omitting it would have very little effect on the regression analyses.

The experimental E_p data for the first reduction waves are given in Table I. The data fall into three groups, depending upon the number of ortho chlorines, which cause the nitro group to twist out of the plane of the ring by either 40° or 65°.

Table I. Peak Potentials (E_p) for the First Reduction Wave of the Chlorinated Nitrobenzenes[a]

no ortho Cl		one ortho Cl		two ortho Cl's	
compd	E_p, mV	compd	E_p, mV	compd	E_p, mV
	−1053	2	−1026	26	−1094
3	−931	23	−930	236	−1010
4	−965	24	−939	246	−1016
34	−875	25	−898	2346	−949
35	−808	234	−876	2356	−934
345	−770	235	−823	23456	−892[b]
		245	−838		
		2345	−784		

[a] For 0.5 mM solution in Me_2SO with 0.1 M TEAP, E_p measured vs. saturated aqueous silver|silver chloride reference electrode at 25 °C. [b] This reduction is irreversible; all others are reversible one-electron processes.

Table II. Hammett $\rho\sigma$ Correlations Using Primary σ Constants[a]

	with all data			data without adjacent chlorines		
o-Cl's	0	1	2	0	1	2
no. of compd	6	8	6	4	3	2
$\sigma = 0$, mV	−1042	−1057	−1160	−1049	−1094	−1230
ρ_e, mV	293	245	201	327	349	339
r	0.933	0.976	0.987	0.998	0.998	1
s, mV	12.1	16.7	11.7	5.9	4.3	0

[a] $\sigma_o = 0.20$, $\sigma_m = 0.37$, $\sigma_p = 0.23$.

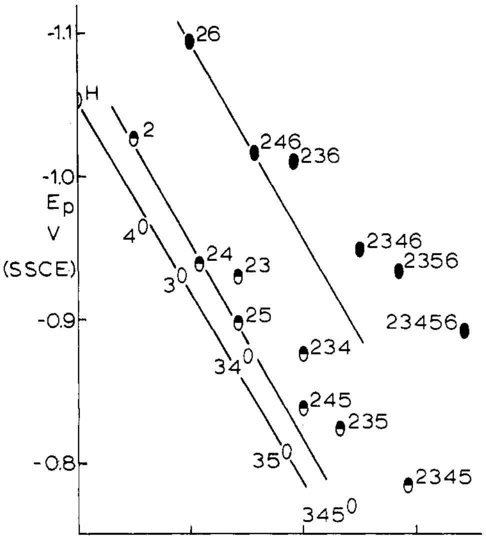

Figure 2. Correlation of E_p data vs. sum of Hammett σ constants: size of ellipses indicate limits of uncertainty; lines indicate limiting maximum slopes for related data; for chlorine $\sigma_o = 0.20$, $\sigma_m = 0.37$, $\sigma_p = 0.23$. The open, half-filled, and filled ellipses designate compounds with zero, one, or two ortho chlorines, respectively.

Hammett Correlation with Primary σ Constants. Since primary σ values are generally used in Hammett correlations of electrochemical data, we initially used these values for chlorine ($\sigma_m = 0.37$, $\sigma_p = 0.23$, and $\sigma_o = 0.20$) in a plot of all three sets of E_p data relative to σ as seen in Figure 2. There is always some question as to the value of σ_o since a steric effect is present. Previous workers have used $\sigma_o = \sigma_p = 0.20$ or 0.23.[11a,b] A change in the σ_o value should be reflected mainly as change in the steric offset of the E_p data. Table II summarizes the Hammett correlation and gives the degree of statistical significance. The reaction constant ρ_e is expressed in millivolts, which is usual for electrochemical data correlations. It can be converted to a Hammett ρ at 25 °C by dividing ρ_e by 59.16

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Table III. Empirical Determination of Adjacent Chlorine Correction Factor, σ_α[a]

o-Cl's	0	1	2
sets of adj Cl's	3	8	9
av dev, mV	-20.2 ± 1.8	-34.4 ± 9.8	-35.3 ± 6.8
ρ_e, mV	327	349	339
σ_α[b]	-0.062 ± 0.006	-0.099 ± 0.028	-0.104 ± 0.020

[a] $\sigma_o = 0.20$, $\sigma_m = 0.37$, $\sigma_p = 0.23$, $\sigma_\alpha = (\text{av dev})/\rho_e$.
[b] $\sigma_\alpha(\text{av}) = -0.096 \pm 0.015$.

Table IV. Reevaluation of Hammett Correlation Using the Empirical σ_α(av) Correction[a]

	with $\sigma_p = 0.23$ and $\sigma_\alpha = 0.096$			with $\sigma_p{}^\circ = 0.27$ and $\sigma_\alpha = 0.088$		
o-Cl's	0	1	2	0	1	2
$\sigma = 0$, mV	−1052	−1093	−1223	−1055	−1087	−1216
ρ_e, mV	346	343	324	337	321	303
r	0.996	0.991	0.988	0.9994	0.997	0.997
s, mV	9.1	10.2	11.3	3.6	5.5	5.5

[a] $\sigma_o = 0.20$, $\sigma_m = \sigma_m{}^\circ = 0.37$.

mV. When all the data are used, the ρ_e appears markedly altered by the steric effect of the ortho chlorines, with a 30% decrease for the 2,6 compounds. While the correlation coefficient indicate a good fit (r's > 0.976), the standard deviations for the data points are 2 to 3 times the expected maximum experimental error of ±5 mV, which suggests the fit should be better if the σ values are truly additive. In comparison to the limiting slopes for the three sets of data shown in Figure 2, compounds with adjacent chlorines all tend to have more negative reduction potentials, or conversely the sum of σ constants is more positive than that required. It is also apparent that the more sets of adjacent chlorines a compound has the greater its dispersion is from the limiting slope. An analysis of data from compounds with no adjacent chlorines is included in Table II and shows that the ρ values are consistent within 7%. Since the number of data sets are limited to four or less, the correlation coefficients are excellent but not very significant. However, the standard deviations are about the same as the expected experimental error.

σ_α Correction. The preceding results suggest that an empirical correction in σ for each pair of adjacent chlorides might improve the correlation of E_p with σ for all the data. For each set of compounds a correction constant σ_α was found by dividing the average deviation per adjacent chlorine pair by the reaction constant ρ_e. As seen in Table III, the three σ_α terms are quite similar, and an average value was calculated equal to −0.096. Note that this constant is based on a total of 20 adjacent chlorine interactions in 11 compounds out of a total set of 20 nitrobenzene compounds. A plot of E_p vs. $\Sigma\sigma$ which includes σ_α corrections for each pair of adjacent chlorines is given in Figure 3. The correlations look quite good, with ρ values within 8% for the different sets of data, indicating that *with the applications of one correction factor the substituent constants for Cl are truly additive.* However, in Table IV we see that the standard deviation for the dispersion of the data is about 4–6 mV greater than that expected for the quality of voltammetric data. A study of Figure 3, which is supported by the dispersion data, shows that all the compounds with para chlorines are dispersed to the lower side of the regression lines, while all those without that chlorine are found slightly above and right of the lines. This result indicates that the σ_p constant is too small relative to σ_m, which may account for the excessive standard deviation in Table IV.

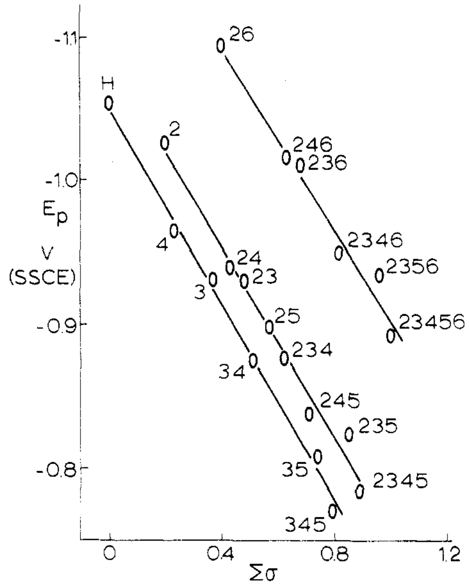

Figure 3. Correlation of E_p data vs. sum of Hammett σ constants plus corrections for adjacent chlorine interactions, $\sigma_\alpha(\text{av}) = -0.096$; substituent constants same as in Figure 2.

Normal Substituent Constants σ°. Since half of the compounds investigated have para chlorines, the correction in the σ_p value can be calculated from the average deviation (7.2 mV) of all the para chloro compounds from the regression line. The correction factor, $\Delta\sigma_p = 2(\text{av dev})/\text{av}\ \rho_e$, is found to be 0.043. Thus, for a para chlorine a better σ_p value is 0.23 + 0.043, or 0.273, which is the *same as the normal substituent constant* ($\sigma_p{}^\circ = 0.27$), obtained for reaction in which there is no resonance interaction of chlorine with the reaction center.[15] Because $\sigma_m{}^\circ = \sigma_m$, it seems that normal σ constants (σ°) are the appropriate ones to use in this correlation of electrochemical potentials. (See the Discussion section.) The appropriate value for $\sigma_o{}^\circ$ is open to question, as several have been calculated and compared,[16] and it ought to be equal to or greater than $\sigma_p{}^\circ$. However, the actual value of $\sigma_o{}^\circ$ is most critical in determining the magnitude of the steric effect or potential offset due to ortho chlorines, as the regression lines are nearly parallel.

Hammett Correlation Using $\sigma_p{}^\circ$, $\sigma_m{}^\circ$, and σ_o. With $\sigma_p{}^\circ = 0.27$ and $\sigma_o = 0.20$, we repeated the analysis procedures used before and found a new average σ_α of −0.088, which represents a 7% decrease from the original value. A new Hammett $\rho\sigma$ correlation was carried out, and the results are given in Table IV. The ρ values have decreased slightly but remain nearly equal. The correlation coefficients are remarkably good, being ≥0.997, and most importantly the standard deviations are about as expected from our experimental accuracy.

Discussion

Rationale for Using σ° Constants. Primary σ constants have been used in previous Hammett $\sigma\rho$ correlations of electrochemical data, except where σ^- gives a better fit for conjugated electron-withdrawing substituents like NO_2 and CO_2R.[11c] The results of the present study show that σ° is appropriate for the para chloro substituent. Why should σ° constants apply to the reduction of nitrobenzenes when they are based on model reactions of substituted phenylacetic acids and derivatives, which do not

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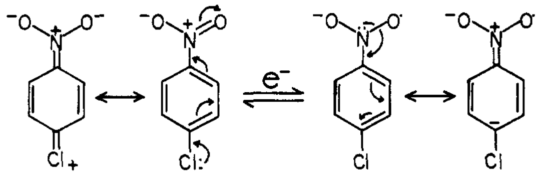
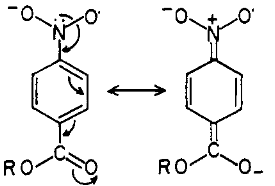
allow for direct conjugation through a π system of the reaction center with the substituent? The question may be answered by looking at how, in this reversible electrochemical reaction, the chlorine substituents modify the energy difference between the reactant (neutral molecule Ia,b) and the product (radical-anion IIa,b). In the neutral molecule there is resonance of a chlorine lone pair of electrons with the nitro group as depicted by the charge-separated canonical structure Ia, which reduces the expected inductive effect of the chlorine. Put another way, the highest occupied molecular orbital (HOMO) involves some π bonding between the chlorine and the nitro group through the benzene ring. In the electrochemical reduction an electron is added to the lowest unoccupied molecular orbital (LUMO) of the neutral molecule and the HOMO is not involved, except for a slight perturbation. The radical anion so generated still contains the molecular orbitals of the neutral molecule which will contribute little if any to changing the energy difference between the two species. However, the negative charge of the radical anion is delocalized into the ring and the inductive effect of the chlorine helps disperse it further, which helps "stabilize" or lower the energy of the radical anion. The canonical structures IIa and IIb indicate that direct π resonance is not allowed with the chlorine in the radical anion. In other words, the HOMO of the radical anion is a π orbital which is non- or anti-bonding at the chlorine substituent, and thus only the inductive effect of the chlorine is operating. The overall result is similar to the system used to define σ°, where direct resonance between the substituent and the reaction center is blocked. Except in this case, the substituent is not allowed effective resonance with the ring, while in the model case the reaction center is not allowed resonance with the ring due to the methylene group. Thus, it seems that σ° values are justified for the electrochemical reduction of chlorinated nitrobenzenes. If our rational is correct, then one would expect that σ° constants are appropriate for other reversible electrochemical reductions where the substituent loses its ability for resonance with the reaction center in the radical anion, for example, with halogenated aryl carbonyl and nitroso compounds. However, σ^- has been found appropriate for para substituents like carboxylate and nitro, where resonance is enhanced with the reaction center in the radical-anion (III) species.



Ia Ib IIa IIb



III

Logical Basis for the σ_α Correction. Substituents like chlorine, when π-bonding interactions are not allowed, delocalize negative charge (electron density) from a reaction center by their inductive effect. The effectiveness of this process is σ_α to their σ constant as determined from monosubstituted model systems. The σ constant not only incorporates the effective electronegativity of the group but also depends on the relative availability of electron density at the adjoining carbon which makes the constants position dependent. A chlorine substituent, due to its large electronegativity, will develop a fairly strong dipole along its bond. Adjacent chlorines, which are at the usual bond lengths and angles found in aromatic compounds, are at <0.9 of their combined van der Waals radii (Table V) from each other. Thus, they would experience a strong electrostatic repulsion due to the localized charge of the adjacent dipoles. This field effect should result in some changes from the normal parameters expected for a single substituent (upon which the σ constants are based). Bond stretching and bending are possible, as well as reduction in the amount of charge the substituent can accommodate. These factors, particularly the last one, would be responsible for the empirical σ_α correction which we found. The overall result is that two adjacent chlorines are not as effective as two separate chlorines in withdrawing electron density from an aromatic ring.

Table V. Calculated Interatomic Distances and Related van der Waals Interactions of Selected Atoms in Chlorinated Nitrobenzenes[a]

adjacent non-bonding atoms	twist of NO_2 group, deg	interatomic distance, Å	% of van der Waals radii
H, Cl	0	2.84	95
H, N	0	2.69	100
H, O	0	2.49	96
Cl, Cl	0	3.09	86
Cl, N	0	2.99	91
Cl, O	0	2.53	79
Cl, O	30	2.66	83
Cl, O	40	2.77	87
Cl, O	60	3.03	95
Cl, O	65	3.10	97
Cl, O	90	3.47	108

[a] Based on idealized model: all angles 120 °; bond lengths and effective van der Waals radii from tables in Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; pp 107, 109.

Separation of σ_α(av) into Two Terms and the Dependence on σ_o° Value. Unless σ_o° is equal to σ_p°, it is unlikely that the correction factor σ_α is the same for the ortho,meta and the meta,para pairs of chlorines. Thus, it seems reasonable to separate σ_a into two terms, σ_α(om) and σ_α(mp), which reflect in some way the σ values for the ortho, meta, and para positions.

The simplest approach is to make the correction terms proportional to the average of the σ constants for the adjacent chlorines

$$\sigma_\alpha(\mathrm{om}) = a(\sigma_o^\circ + \sigma_m^\circ)/2 \qquad (1)$$

$$\sigma_\alpha(\mathrm{mp}) = a(\sigma_m^\circ + \sigma_p^\circ)/2 \qquad (2)$$

where a is the proportionality constant which is assumed to be the same in both equations. Now since σ_α(av) is based on 10 ortho,meta pairs and 10 meta,para pairs of interactions in 11 compounds:

$$2\sigma_\alpha(\mathrm{av}) = \sigma_\alpha(\mathrm{om}) + \sigma_\alpha(\mathrm{mp}) \qquad (3)$$

Thus

$$\sigma_\alpha(\mathrm{om}) = 2\sigma_\alpha(\mathrm{av})/[1 + (\sigma_m^\circ + \sigma_p^\circ)/(\sigma_o^\circ + \sigma_m^\circ)] \qquad (4)$$

$$\sigma_\alpha(\mathrm{mp}) = 2\sigma_\alpha(\mathrm{av})/[1 + (\sigma_o^\circ + \sigma_m^\circ)/(\sigma_m^\circ + \sigma_p^\circ)] \qquad (5)$$

Since σ_α(av), σ_m°, and σ_p° are known quantities, the values of the correction factors σ_α(om) and σ_α(mp) depend on the actual value of σ_o°. Therefore a number of σ_o° values were assigned over the range of 0.27–0.57 and corresponding values for σ_α(om) and σ_α(mp) were calcu-

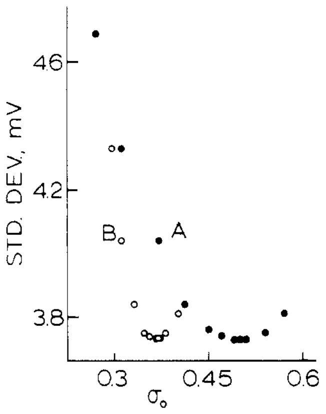


Figure 4. Dependence of standard deviation in $\rho\Sigma\sigma^\circ$ correlations upon value of ortho chlorine σ constant, with separate corrections for adjacent chlorines in ortho,meta and meta,para positions (see text): (a) σ_α is proportional to average of adjacent σ constants, (b) σ_α is proportional to product of adjacent σ constants.

lated. These correction factors were used in a series of Hammett $\rho\sigma$ correlations. Because the standard deviation term is very sensitive to the quality of the correlation, this term was plotted vs. the values chosen for σ_o°. From Figure 4 there is seen a minimum in the standard deviation at $\sigma_o^\circ = 0.50 \pm 0.03$ which corresponds to $\sigma_\alpha(\text{om}) = -0.101$ and $\sigma_\alpha(\text{mp}) = -0.075$, with a proportionality constant a equal to 0.117. The σ_o° value of 0.50 is comparable to the largest value (0.53) calculated for chlorine by Jones and Smith,[16] from data on the ionization of substituted phenylacetic acids in water.[17] It also falls in the range of Taft's σ_I value for a chlorine substituent (0.47[18] or 0.51[19]).

Should there be any correlation between σ_o° and σ_I? Both constants purportedly involve pure inductive effects of the substituent, σ_I being at the 4-position of the bicyclo[2.2.2]octyl carboxylate system. In terms of distance and dipole orientation to reaction center, the substituents are different, but these properties may tend to compensate to make the values of the constants similar. Also Taft[15] has related σ_m° and σ_p° constants to σ_I by a σ_R° term which represents a "falloff" in distributed charge about the ring. There is no reason to equate σ_o° with σ_I, but it is possible that σ_o° could be as large as σ_I since it is reasonable that electron density on the ring would be higher at the ortho position and "fall off" in going to the meta and para positions as indicated by the σ_R term.

However, if the formal σ° constants are really proportional to the amount of charge delocalized by a single chlorine substituent from the ring at various positions, then the correction factors should be related to the actual electrostatic repulsion between the quantities of charge (q) on adjacent chlorines, that is, the electrostatic force $F_e = q_1q_2/r^2$, where r is the separation distance between chlorines which we assume constant. Thus the correction term should be proportional to the product of the substituent constants. In this case, in place of eq 4 and 5, we have

$$\sigma_\alpha(\text{om}) = 2\sigma_\alpha(\text{av})[1 + \sigma_p^\circ/\sigma_o^\circ] \tag{6}$$

$$\sigma_\alpha(\text{mp}) = 2\sigma_\alpha(\text{av})[1 + \sigma_o^\circ/\sigma_p^\circ] \tag{7}$$

The correction factors now depend on the $\sigma_o^\circ/\sigma_p^\circ$ ratio or its inverse. From the correction factors used in the previous series of $\rho\sigma$ correlations a new set of σ_o° values were calculated, using eq 6 and 7. These σ_o° values were plotted against the standard deviations for each correlation (Figure 4) and a sharp minimum is found at $\sigma_o^\circ = 0.37 \pm 0.01$ and again $\sigma_\alpha(\text{om}) = -0.101$ and $\sigma_\alpha(\text{mp}) = -0.075$, but the proportionality constant a' ($= \sigma_\alpha(\text{om})/\sigma_o^\circ\sigma_m^\circ = \sigma_\alpha(\text{mp})/\sigma_m^\circ\sigma_p^\circ$) is 0.744. The σ_o° value is the same as the value calculated by Jones and Smith[16] for chlorine from data on the association of benzoic acids with 1,3-diphenylguanidine. This results supports the concept that σ° constants are proportional to the charge taken on by the substituent and that the σ_α correction is proportional to the product of the adjacent charges. It is interesting that σ_o° and σ_m° are found equal in view of the concept that electron density drops off around the ring from the reaction center. At this time we consider both 0.37 and 0.50 as possible limiting values for σ_o° of chlorine in this system. However, we tend to favor the larger value on the basis of comparisons of proportionality constants a and a' calculated from data of Gassman and Fentiman[7] for σ^+ substituent constant of the 3,5-dichloro-4-cyanophenyl group. They found experimentally the σ^+ to be 1.22, while the sum of the individual σ^+ constants was 1.46, which is equivalent to a $\sigma_\alpha(\text{mp})$ correction of -0.12. For these data a is found to be 0.113 (equivalent to our a) and a' is 0.455 (only 61% of our a'). We currently have molecular orbital calculations under way on chlorinated nitrobenzene radical anions to see if the electron-density distribution is consistent with either of these σ_o° constants.

Possible Variability of the σ_o° "Constants". Since the nitro reaction center adjacent to the ortho chlorine has an appreciable charge, then it should modify the σ_o° value in a way similar to the effect of an adjacent chlorine substituent. That is, the reaction center could increase or decrease the charge localized on the ortho chlorine by its electrostatic (field) interaction, depending upon the sign, magnitude, and location of the charge in the reaction center. The nitrogen atom of a nitro group has a partial positive charge (δ^+) and the oxygens a partial negative charge (δ^-). These partial charges become more negative when an electron is added to form the radical anion. Table V gives interatomic distances and their separations relative to van der Waals radii for the nitro group atoms and ortho chlorine and hydrogen atoms. Most apparent from the data is the greater penetration of oxygen into the van der Waals radii of chlorine than nitrogen and its twist-angle dependency. Thus, the field effect of oxygen should make σ_o° less than "normal", but this effect should be mitigated to some degree by the further twisting of the C–N bond and reductions of the charge on oxygen due to the field effect of the chlorine dipole. When two ortho chlorines are present, σ_o° should be increased since the C–N bond twist is larger, which makes the repulsive term smaller due to the increased chlorine–oxygen distance, and the relative effect of the δ^+ nitrogen should be more pronounced. The fact that adjacent chlorine substituents modify their σ° constants leads to the conclusion that σ_o° values should also depend upon the polarity and distance of atoms in the reaction center and how these properties are modified by the reaction. Due to the complexity of these factors we have not attempted to determine the magnitude of the change the reaction center makes on the σ_o° value for chlorine. Thus, we agree with the ideas put forth by both Shorter[20] and Charton[21] that no single general scale of σ_o values is possible.

Steric Effects of the Ortho Chlorines. When assigning σ_o constants based on a specific reaction, it is generally assumed that $\rho_o = \rho_{m,p}$ for that reaction. For our

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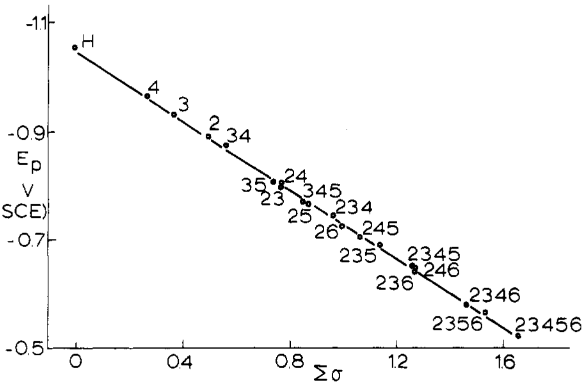

Figure 5. Correlation of E_p data, adjusted to remove steric offset, $\Delta E_s(\text{o}) = -133$ mV and $\Delta E_s(\text{o,o}) = -370$ mV vs. sum of normal σ constants ($\sigma_o{}^\circ = 0.50$, $\sigma_m{}^\circ = 0.37$, $\sigma_p{}^\circ = 0.27$) with corrections for adjacent chlorine interactions, $\sigma_\alpha(\text{om}) = -0.101$ and $\sigma_\alpha(\text{mp}) = -0.075$.

system it appears from Table IV that the ρ values are not quite equal: $\rho_o = 0.96\rho_{m,p}$ and $\rho_{o,o} = 0.93\rho_{m,p}$. The trend of slightly lower ρ values with increasing number of ortho chlorines has persisted throughout our calculations. At one standard deviation a minimum value for the ρ [$\rho_{m,p}$(min)] would be $0.97\rho_{m,p}$, which suggests that the calculated ρ values may really differ (especially in the case of the ortho,ortho compounds) and that the presence of ortho chlorines actually causes a slight increase in the electron density on the nitro group relative to the ring in the radical anion. However, the variation in the three ρ values is nearly within 2 standard deviations and the variation still has some chance of being an artifact of experimental error.

The most notable and expected steric effect of an ortho chlorine is to offset the reduction potentials to more negative voltages. The apparent magnitude of this steric effect (ΔE_s) is a function of the $\sigma_o{}^\circ$ value involved in the correlation. Thus we find a much larger steric effect than that previously noted by Hawley and coworkers[11ab] who used $\sigma_o = \sigma_p = 0.20$ in correlations with mono- and disubstituted chloronitrobenzenes. They also noted an apparent increase in ΔE_s for the 2,3-dichloronitrobenzene, which they ascribed to a "buttressing" effect of the meta chlorine.[13] We believe this effect was a manifestation of the need for the σ_α correction, as we see no evidence for a "buttressing" effect in our corrected data.

Because the reduction potential correlates to the energy level of the radical anion HOMO, the large ΔE_s value is a result of the twist of the nitro group which decreases the π-orbital overlap and raises the HOMO energy level in the hindered radical anion relative to that of a comparable planar species. The ΔE_s values for all the mono-ortho chloro compounds should be constant as they all have approximately the same degree of twist. Likewise all the ortho,ortho chloro compounds are found to have a constant but 2.8-fold larger ΔE_s value, for with a 65° twist the π overlap is greatly reduced. Note, the acutal ΔE_s values among the three sets of data can not be taken simply as their potential difference at $\sigma = 0$ since the calculated slopes are slightly different. Instead the ΔE_s must be determined at the mean σ value for each data set relative to the average slope. Actually we determined ΔE_s relative to the slope obtained for all data after translation of the ortho and ortho,ortho chlorine data sets to give a correlation with a minimum standard deviation, as seen in Figure 5 for $\sigma_o{}^\circ = 0.50$. In this correlation, $\rho_e = 320 \pm 5$ mV, with $r = 0.9995$ and a standard deviation of ±4.3 mV, and $\Delta E_s(\text{o}) = -133$ mV and $\Delta E_s(\text{o,o}) = -370$ mV. When the correlation was determined for $\sigma_o{}^\circ = 0.37$, we found $\Delta E_s(\text{o}) = -90$ mV and $\Delta E_s(\text{o,o}) = -286$ with a $\rho_e = 319 \pm 6$ mV at $r = 0.9922$ and SD = ±4.4 mV. Both these correlations are excellent and show that all the data can fit one ρ value within the limits of our expected experimental error. Thus the slightly different slope seen for the individual data sets may not be real and $\rho_{m,p} = \rho_o = \rho_{o,o}$ can be justified.

This investigation has demonstrated that corrections for the polar interaction of adjacent chlorine substituents are required to make the σ constants additive in Hammett-type correlations. However, it needs to be extended to other substituent and reactions to test its general relevance. Since most σ constants are accurate to no more than ±0.02 units, the corrections should be noticeable for polar substituents with absolute σ values greater than 0.2. This is assuming, on the basis of the proportionality constant a we found, that the correction factor is about 12% of the individual σ constants. These results would increase the predictive accuracy of $\rho\sigma$ correlations for multiple polar substituents and should, for example, be useful in areas where structure–activity relationships are important.

Experimental Section

A conventional cyclic voltammeter was used. The working electrode was a platinum flag with a total area of 60 mm², coated with mercury by the procedure of Enke et al.[22] An aqueous saturated Ag|AgCl reference electrode was separated from the working compartment of a low-volume H cell by a sintered-glass wool plug. A 20-gauge platinum wire coil in the working compartment formed the counter electrode. Solutions were deoxygenated by purging with dry nitrogen prior to recording voltammograms on a Houston Instrument Omnigraphic 2000 X-Y recorder. Experiments were carried out at 25 ± 2 °C with a single sweep rate of 75 mV/s, and no correction for uncompensated IR drop was deemed necessary for substrates at 0.5 mM.

Peak potentials were obtained by interpolating the voltammograms and had a resolution of ±0.5 mm on the chart, equivalent to ±5 mV. While the absolute peak potentials are not known due to the unknown junction potential between the reference electrode and the Me_2SO solutions, the relative potentials between the compounds should be accurate to the above resolution since experiments were carried out in a short period of time under identical conditions.

Reagent grade dimethyl sulfoxide (Me_2SO) was obtained from J. T. Baker Co. and found to contain at least one electroactive impurity which interfered with recording voltammograms. The Me_2SO was purified by refluxing at approximately 75 °C over sodium hydroxide pellets under nitrogen at 10 torr for 2.5 h. This was followed by a vacuum distillation from calcium hydride at about 1 torr with the middle 80% being collected. Within 48 h of this purification and drying procedure, all the solutions were prepared and examined by cyclic voltammetry.

Tetraethylammonium perchlorate (Eastman low halide) was used as supporting electrolyte at 0.1 M. Nitrobenzene and 16 of the chlorinated nitrobenzenes were obtained from commercial sources (Aldrich, Baker, and Fisher). Samples of 2,6-dichloro-, 3,5-dichloro-, 2,3,6-trichloro-, 2,4,6-trichloro-, 3,4,5-trichloro-, and 2,3,4,6-tetrachloronitrobenzene were synthesized by well-known procedures.[23]

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Registry No. Nitrobenzene, 98-95-3; 3-chloronitrobenzene, 121-73-3; 4-chloronitrobenzene, 100-00-5; 3,4-dichloronitrobenzene, 99-

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54-7; 3,5-dichloronitrobenzene, 618-62-2; 3,4,5-trichloronitrobenzene, 20098-48-0; 2-chloronitrobenzene, 88-73-3; 2,3-dichloronitrobenzene, 3209-22-1; 2,4-dichloronitrobenzene, 611-06-3; 2,5-dichloronitrobenzene, 89-61-2; 2,3,4-trichloronitrobenzene, 17700-09-3; 2,3,5-trichloronitrobenzene, 34283-94-8; 2,4,5-trichloronitrobenzene, 89-69-0; 2,3,4,5-tetrachloronitrobenzene, 879-39-0; 2,6-dichloronitrobenzene, 601-88-7; 2,3,6-trichloronitrobenzene, 27864-13-7; 2,4,6-trichloronitrobenzene, 18708-70-8; 2,3,4,6-tetrachloronitrobenzene, 3714-62-3; 2,3,5,6-tetrachloronitrobenzene, 117-18-0; 2,3,4,5,6-pentachloronitrobenzene, 82-68-8.

Zinc Chloride Catalyzed Decomposition of 1,2-Dihydronaphthalene at 165 °C. A Coal-Related Model Compound Study

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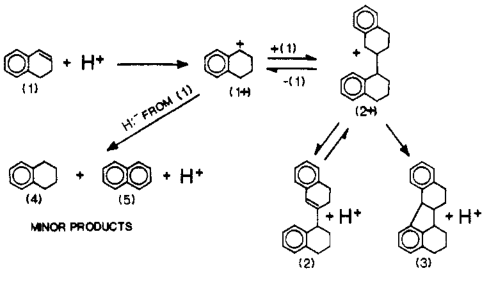
The zinc chloride catalyzed decomposition of 1,2-dihydronaphthalene (1) at 165 °C produces dimers of 1, tetralin, and naphthalene. Zinc chloride functions as a Friedel–Crafts type catalyst by coordinating with a hydroxyl from a water molecule and releasing a proton which initiates a carbonium ion reaction. The stoichiometric role of water has been established by measuring the activity of the zinc chloride–water complex as a function of the degree of hydration of the zinc chloride. The activity maximum occurs at a zinc chloride/water mole ratio of 1:1. Deuterium tracer experiments corroborate the role of water and also verify that the reaction occurs by a carbonium ion mechanism. The carbonium ion nature of the reaction is also inferred by the structures of the products. The 300-MHz ^{1}H NMR spectra of the dimer products are consitent with the previously reported structures of the compounds.

Zinc chloride is used as a catalyst for the hydrogenation of coal[1] and polycyclic aromatic hydrocarbons,[2] but the mechanism of its catalytic action has not been fully established.[3] Because of the importance of coal hydrogenation, a more complete understanding of the zinc chloride catalysis mechanism is also important. Most coal hydrogenations are carried out at thermolytic temperatures, and reactions other than hydrogenation occur concurrently, e.g., pyrolysis and reactions that can be catalytically initiated at subthermolytic temperatures. The latter reactions would proceed at accelerated rates at thermolytic temperatures. A knowledge of these concurrent reactions, some of which constitute the subject of this study, is a necessary background to the understanding of the hydrogenation chemistry.

In this paper the zinc chloride catalyzed subthermolytic decomposition of the coal-related model compound 1,2-dihydronaphthalene (1) is reported. Compound 1 was chosen as the model for the following reasons: (a) it is a hydro aromatic compound, and hydro aromatic structures are believed to be prevalent in coal;[4] (b) its decomposition is catalyzed by zinc chloride;[5] (c) it is the most thermodynamically stable of the possible dihydronaphthalenes, thus eliminating possible rearrangements from less stable to more stable isomers; (d) it contains an alkene-type double bond, which serves two useful purposes. The double bond renders the molecule suitable for future hy-

Scheme I

$$H_2O + ZnCl_2 \rightleftharpoons H^+ + HOZnCl_2^-$$



MAJOR PRODUCTS

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(5) Unpublished work of R.R.B. and L.L.A. has shown that (a) 1,2-dihydronaphthalene decomposes thermally in the absence of zinc chloride, (b) the rate of the thermolytic reaction is greatly accelerated in the presence of zinc chloride, and (c) in the presence of zinc chloride, reaction occurs at temperatures below where the uncatalyzed thermolytic reaction has ceased.

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