

acids, in proportions about 5:4, respectively. The oil was dissolved in a small amount of chloroform and, at its boiling point, petroleum ether was added; upon cooling, white crystals of methyl 4-methoxy-2,6-dinitrobenzoate separated: mp 104–105 °C; IR (cm^{-1} , KBr) 1750 (C=O), 1550 and 1350 (NO_2); MS, *m/e* (relative intensity, composition) 256 (11, $\text{C}_9\text{H}_8\text{N}_2\text{O}_7$), 225 (100, $\text{C}_8\text{H}_6\text{N}_2\text{O}_6$), 179 (11, $\text{C}_8\text{H}_5\text{NO}_4$); ^1H NMR (CDCl_3) δ 7.7 (2 H, Ar H), 3.8 (6 H, OMe).

4-Methoxy-2,6-dinitrobenzoic acid (Io) was obtained by saponification of its methyl ester by methanolic sodium hydroxide. The acid was recrystallized from benzene: mp 179–180 °C; IR (cm^{-1} , KBr) 2400–3300 (OH) 1725 (C=O), 1550 and 1350 (NO_2); MS *m/e* (relative intensity, composition) 242 (50, $\text{C}_8\text{H}_6\text{N}_2\text{O}_7$), 227 (35, $\text{C}_7\text{H}_3\text{N}_2\text{O}_7$), 210 (42, $\text{C}_7\text{H}_2\text{N}_2\text{O}_7$), 198 (30, $\text{C}_7\text{H}_6\text{N}_2\text{O}_5$), 179 (20, $\text{C}_7\text{H}_3\text{N}_2\text{O}_4$), 122 (100, $\text{C}_6\text{H}_4\text{NO}_2$); UV λ_{max} (water) 210 nm ($\log \epsilon$ 4.32). Anal. Calcd for $\text{C}_8\text{H}_6\text{N}_2\text{O}_7$: C, 39.68; H, 2.50; N, 11.57. Found: C, 39.9; H, 2.71; N, 10.98.

Expected Products of Decarboxylation. **5-Iodo-1,3-dinitrobenzene (Vi)**, mp 101–102 °C, was obtained by iodination of *m*-dinitrobenzene, by following the method of Arotzky and Butler.³¹ **1-Bromo-3,5-dinitrobenzene (Vb)**, mp 76–77 °C, was made by bromination of *m*-dinitrobenzene, by following the method of Derbyshire and Waters.³⁰ **3,5-Dinitroanisole (Vo)** was prepared by the action of sodium methoxide on 1,3,5-trinitrobenzene.³⁶

Products of Decarboxylation. Dilute solutions, ca. 1.5 L at concentration of $(1-2) \times 10^{-4}$ M, of carboxylic acids of series I and II were heated in sealed vessels at 125 °C for 8–10 decarboxylation half-lives, as determined by kinetic measurements. The cooled contents of the vessels were extracted 5 times with 100-mL portions of methylene chloride. Evaporation of the extracts in each case but two left a residue which was shown by its MS and ^1H NMR spectra and its TLC behavior (MeOH/chloroform, 1/4) to be identical with an authentic sample of the anticipated decarboxylation product. In regard to chloro substrates Ic and Iic, no authentic 1-chloro-3,5-dinitrobenzene was synthesized; the residues after reaction showed spectra characteristics expected of this compound. The product from 2-methoxy-4,6-dinitrobenzoic acid (Iio) was not 3,5-dinitroanisole but rather a solid with TLC R_f similar to the R_f for 2-hydroxy-4,6-dinitrobenzoic acid.

Kinetic Measurements. Each decarboxylation reaction was examined preliminarily by heating portions of an aqueous solution of it, sealed in glass, for varying periods of time at a temperature expected to be conducive to decarboxylation. UV-vis spectra of

the resulting solutions were recorded. In every case two significant features were noted: the final spectrum differed significantly from the initial in absorbance at one or more wave lengths and there were well-defined isosbestic points. A wavelength at which absorbance changed significantly during reaction (usually in the range 220–250 nm) was chosen for monitoring of reaction in kinetic runs.

For temperatures up to 150 °C, liquid thermostat baths were used; temperature variation was about $\pm 0.1^\circ$. For higher temperatures, a temperature-controlled “bath” of fluidized aluminum oxide, with a variability of ca. $\pm 0.5^\circ$, was employed.

Solutions of carboxylic acids in series I and II, ca. 1×10^{-4} M in deionized water, were apportioned in 5-mL aliquots into glass ampules which were then sealed. For runs at temperatures up to 150 °C, thin-walled, flat-bottomed ampules such as used to package medicinal drugs were used, but heavy-walled glass ampules were used at higher temperatures. The ampules for a run, usually 15 in number, were placed in the thermostat all at once and single ampules were removed at recorded times, mostly during the first 4 half-lives. Upon removal from the thermostat at less than 150 °C, ampules were immediately plunged into cold water, while ampules removed from the hotter thermostat were placed in a stainless steel beaker and allowed to cool. The absorbance of the solution within each ampule was determined at the chosen wavelength. Plots of $\ln(A_t - A_{\text{inf}})$ vs. time were linear without exception; for evaluation of first-order rate constants, the negatives of the slopes calculated by a weighted least-squares procedure were taken, the weighting factor being $(A_t - A_{\text{inf}})^2$. (A_t is absorbance at time t and A_{inf} is the absorbance at “infinity”; for very slow runs, A_{inf} was calculated by use of a computer.)

Enthalpies and entropies of activation were reckoned by means of standard expressions.³⁷

Solvent Isotope Effect Experiments. Reaction solutions were prepared in the usual way and placed in standard square cuvettes which were tightly capped but not sealed. Kinetic runs were performed in a Perkin-Elmer 559A spectrophotometer, which has a thermostated cell compartment, a cuvette holder with room for five cuvettes, and records absorbances automatically as programmed. (We thank Prof. C. F. Bernasconi for permission to use this instrument.) During each set of determinations, there were concurrently within the cell compartment two cuvettes with ordinary water and three with deuterium oxide solvent. Reactions were followed for about 2 half-lives. Their rate constants, reckoned from absorbance change in the usual way, are listed in Table IV.

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Simultaneous Use of Empirical and Semiempirical Substituent Parameters as a New Method of Analysis of the Ortho Effect. Application in Reactions via Aryl Anion Intermediates¹

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Received November 13, 1984

A new method to estimate ortho parameters suitable to factor the ordinary electronic effect in the correlation analysis of the ortho effect is described. It is based on calculated MO energies of appropriate isodesmic processes. The superiority of the use of these semiempirical ortho parameters, compared with the current method of Fujita and Nishioka, is illustrated by analysis of the ortho effect in three reactions for which aryl anion intermediates have been postulated. A qualitative theoretical interpretation of the separation between ordinary and proximity electronic effects is given.

The peculiar behavior of ortho-substituted benzene derivatives in chemical reactivity, chemical equilibrium,

and other properties, compared with that of the corresponding para- and meta-substituted compounds, is usu-

ally referred to as the ortho effect. Most approaches to a quantitative understanding of this effect are based on correlation analysis of the type known as linear free energy relationships (logarithms of experimental rate or equilibrium constants on each side of the equation).³ Among the different approaches, those based on a one-parameter correlation of the classical Hammett type (eq 1) have

$$\log k_o = \rho\sigma_o + c \quad (1)$$

failed, because no reaction of ortho-substituted compounds has been found that is exempt from proximity effects; the search for a single, generally applicable scale of such σ_o seems futile.³

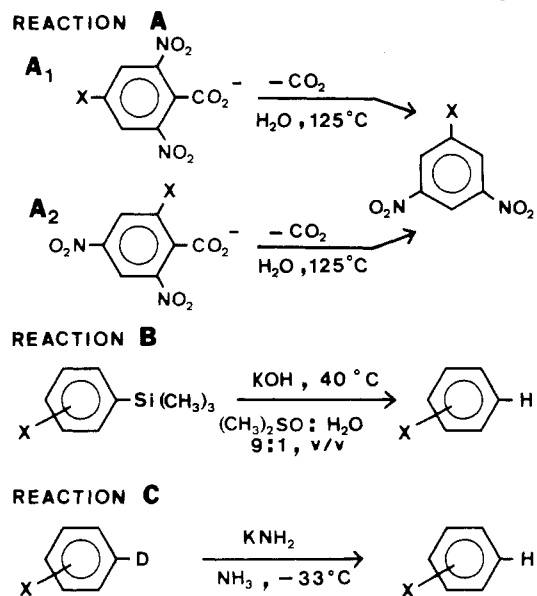
One of the multiparameter approaches is that of Charton,⁴ in which he concludes that there is no steric contribution to the ortho effect. His analysis has been criticized,³ because the compounds with the bulkiest substituents (*t*-Bu, CF₃, I, NO₂), as well as the unsubstituted compound, were systematically excluded from the correlations. The original approach of Krygowski and Fawcett,⁵ based on an attempted separation between enthalpic and entropic contributions, gave poor results with the data of the accompanying paper¹ and will not be considered here. The recent introduction of new ortho steric parameters by Gallo,⁶ Mager,⁷ and Dash⁸ has not changed the situation much. The so-called ortho effect remains poorly understood.

Although not exempt from problems (see below), the approach that seems most promising to us is the one of Fujita and Nishioka.⁹ According to their model, the total effect of ortho substituents is expressed (eq 2) by the

$$\log k_o = \rho\sigma_o + f(\sigma_F)_o + \delta(E_s)_o + c \quad (2)$$

addition of terms for the steric effect (factored by a suitable steric parameter, originally the E_s of Taft-Kutter-Hansch), the "proximity electronic effect"¹⁰ (factored by a suitable field effect parameter, σ_F),¹² and the "ordinary electronic effect".¹⁰ The latter is defined as the effect

Scheme I. Three Reaction Series via Aryl Anion Intermediates Whose Ortho Effect Is Here Analyzed



corresponding to imaginary conditions in which the other two effects are negligible; it should be factored by a σ_o parameter, analogous to σ_m and σ_p . The important novelty of this approach is that, if meta and para compounds follow a Hammett-type equation (eq 3), then all three series of

$$\log k_{m,p} = \rho\sigma_{m,p} + c \quad (3)$$

$$\log k_{o,m,p} = \rho\sigma_{o,m,p} + f(\sigma_F)_o + \delta(E_s)_o + c \quad (4)$$

reactions can be included simultaneously in the same correlation (eq 4). One or two terms in the correlation might be statistically nonsignificant; in that case, the corresponding effects are negligible.

Given the unavailability of suitable σ_o parameters, Fujita and Nishioka tentatively assumed $\sigma_o \equiv \sigma_p$ (or $\sigma_o \equiv \sigma_p^o$ or σ_p^- or σ_p^+) depending on which σ_p scale is the best to correlate the data for meta- and para-substituted compounds). They were aware that this assumption may underestimate the polar component of the ortho substituents. They claim that this underestimation is taken into account by the "proximity electronic effect".

Although the Fujita-Nishioka model is reasonably well-known,¹⁵ it has been applied little outside the authors' laboratory. Nowadays avoidance of it cannot be imputed to the difficulty of the statistics involved. It should be stressed that, even if a correlation of the type of eq 4 were statistically significant, to be chemically significant it has to give a ρ value close to the ρ value obtained in the correlation of eq 3, with only meta and para compounds. In the context of our investigation of the ortho effect in the decarboxylation of dinitrobenzoate ions (accompanying paper), we applied the Fujita-Nishioka model and obtained an odd result: the apparent complete absence of a steric effect (despite the bulkiness of a strongly hydrated carboxylate group). This, and the important deviation of the ρ value obtained in eq 4 with respect to the one obtained in eq 3, makes us suspect that the assumption $\sigma_o \equiv \sigma_p$ makes the proximity electronic effect unrealistically high, to the detriment of the steric effect, thus blurring the global pattern of substituent effects.

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(9) (a) Fujita, T.; Nishioka, T. *Prog. Phys. Org. Chem.* 1976, 12, 49-48.

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(10) Fujita and Nishioka used originally the terms "proximity polar effect" and "ordinary polar effect", as recommended by the editors of ref 3 and 23. However, we prefer to use the term *electronic* instead of *polar*, following the IUPAC recommendations (ref 11) and the current practice (ref 14 and 40).

(11) "Glossary of terms used in Physical Organic Chemistry", IUPAC Recommendations 1982, *Pure Appl. Chem.* 1983, 55, 1281-1371.

(12) Originally, Fujita and Nishioka used the Swain-Lupton-Hansch *F* parameters, because at that time the Hansch compilation of *F* values was much more complete than the one of σ_1 by Taft. Nowadays, a very complete compilation of σ_1 has been published by Charton (ref 13), and we think that the use of these parameters in the correlation of eq 4 is more consistent with the use of several resonance scales (σ_R , σ^o_R , σ^+R , σ^-R) than the use of *F* parameters. In any case, we have verified that the consequence of the analysis is similar whichever set of parameters is employed. We use the symbol σ_F for the old σ_1 , following a recent proposal (ref 14).

(13) Charton, M. *Prog. Phys. Org. Chem.* 1980, 13, 119.

(14) Reynolds, W. J. *Prog. Phys. Org. Chem.* 1983, 14, 165.

(15) The work of ref 9a has been cited more than 50 times, according to the on-line version of *Science Citation Index*.

Table I. Relative Rate Constants Corresponding to the Reactions of Scheme I and ab Initio Calculated Energies for the Isodesmic Process of eq 5

X	reaction A ^a		reaction B ^b			reaction C ^c			$-10^4\Delta E$ for eq 5, ^d au		
	$\log(k_{rel})_o$	$\log(k_{rel})_p$	$(k_{rel})_o$	$(k_{rel})_m$	$(k_{rel})_p$	$(k_{rel})_o$	$(k_{rel})_m$	$(k_{rel})_p$	o	m	p
NO ₂									482	347	417
CN									314	275	369
CF ₃				480		6×10^5	10^4	10^4	228	158	174
F			4000	108	8.0	4×10^6	4×10^3	2×10^2	133	103	39
Cl	3.194	0.984	3960	400	34.5				295	228	198
Br	3.358	0.993		726	50.5				(295) ^e		
I	2.859	0.887							(195) ^f		
H	0.000	0.000	1.0	1.0	1.0	1.0	1.0	1.0	0	0	0
Me			0.60		0.265	0.2	0.4	0.2	2	-4	-18
OMe		-0.193	6.3	2.17	0.24	500	1	0.5	60	52	-22
NMe ₂			14	0.131	0.026	1.4	0.2	0.07	-34 ^g	-30	-135
Ph				3.84	2.49	4.7	3.3	2.9			
OPh							50	4			
t-Bu								0.2			
Et				0.40							

^a Reference 1. ^b Reference 18. ^c Reference 19. ^d Reference 22. ^e Assumed equal to the value for Cl. ^f Estimated value (see text). ^g Value for NH₂.

In contrast, our kinetic results correlate with calculated MO energies more successfully than with any empirical parameter. This has prompted us to introduce a semi-empirical method for estimating the σ_o to be used in correlations of the type of eq 4. In order to assess broadly the usefulness of this new method, we have applied it also to analysis of the ortho effect in two other reactions for which aryl anion intermediates have been postulated.

Besides the matter of which are the best parameters to use in eq 4, there is the basic theoretical question of what is the nature of the so-called "ordinary" and "proximity electronic effects". We provide a qualitative answer.

Methods and Results

Ortho Effect in Reactions via Aryl Anion Intermediates. Aryl anions have been postulated as intermediates in relatively few reactions,¹⁶ among which there are only two sets of kinetic data that include enough substituted compounds to allow a correlation analysis of the ortho effect, namely, the alkaline cleavage of substituted phenyltrimethylsilanes in Me₂SO/H₂O, 9:1, v/v (reaction B of Scheme I),¹⁸ and the H/D exchange of substituted benzenes with potassium amide in liquid ammonia (reaction C of Scheme I).¹⁹ To these two, our results on the decarboxylation of substituted dinitrobenzoate ions in water have to be added (reaction A of Scheme I).¹ In Table I the kinetic data available for these three reactions are collected.

The precision of the experimental kinetic data for reactions B and C is low; most of the rate constants have only

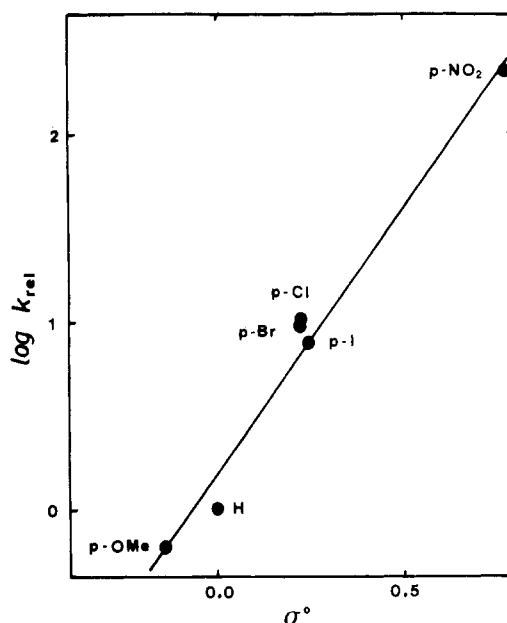


Figure 1. Plot of $\log(k_{rel})_p$ of reaction A vs. σ_p substituent parameters.

one or two significant figures, and some are only rough orders of magnitude. The rate equations for these two reactions are not well defined: the authors recognize that the concentration of base (KOH or KNH₂, respectively) has a marked effect on the reaction rate, but they did not quantify this dependence. Besides, both sets of data include results from two different laboratories.

Although fewer, our results for reaction A are much more precise: interpolated values of $\log k_p$ and $\log k_o$ at 125.0 °C were calculated from very significant Eyring plots, the average standard errors being ± 0.011 and ± 0.020 , respectively (Tables I and II of the accompanying paper). The differences, $\log k_p(X) - \log k_p(H)$ and $\log k_o(X) - \log k_o(H)$, are the $\log k_{rel}$ shown in Tables I and will be considered to belong to the same reaction series. The admissibility of this procedure, unquestionable if the 2,6- and 2,4-nitro groups were absent, is justified in the Appendix to the present paper. There it is shown that the $\log k_{rel}$ calculated in that way reflect only the effects of the X substituent, because the effects of the two extra nitro groups (necessary to make the reaction feasible) cancel out.

Calculated Energy as Explanatory Variable. The regression of $\log(k_{rel})_p$ of reaction A over the classical

(16) To our knowledge, only in the following: reactions of aryl halides catalyzed by bases (ref 17a); alkali cleavage of 2,6-dihalobenzaldehydes (ref 17b); cleavage of *o*-halobenzophenones by potassium amide in liquid ammonia (ref 17c,d); thermal decarboxylation of several aromatic carboxylic acids (ref 17e); hydrogen isotope exchange of fluoro (ref 17f) and nitro (ref 17g) substituted benzenes with sodium methoxide in methanol.

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(19) (a) Hall, G. E.; Piccolini, R.; Roberts, J. D. *J. Am. Chem. Soc.* 1955, 77, 4540-4543. (b) Shatenshtein, A. I. *Tetrahedron* 1962, 18, 95-106. (c) Hall, G. E.; Libby, E. M.; James, E. L. *J. Org. Chem.* 1963, 28, 311-314.

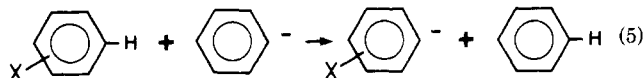
Table II. All Substituent Parameters Used in the Correlations of This Work: σ_o° Are the Semiempirical Ortho Parameters Calculated by eq 6; the Rest Are Literature Values^a

X	σ_o°	σ_m	σ_p°	σ_F	σ_R°	E_s
NO ₂	0.95	0.71	0.77	0.67	0.10	-2.52 ^b
CN	0.62	0.62	0.65	0.57	0.08	-0.51
CF ₃	0.45	0.46	0.51	0.40	0.11	-2.40
F	0.26	0.34	0.10	0.54	-0.44	-0.46
Cl	0.58	0.37	0.22	0.47	-0.25	-0.97
Br	0.58	0.37	0.22	0.47	-0.25	-1.16
I	0.39	0.34	0.24	0.40	-0.16	-1.40
H	0.00	0.00	0.00	0.00	0.00	0.00
Me	0.004	-0.06	-0.17	-0.01	-0.16	-1.24
OMe	0.12	0.11	-0.14	0.30	-0.44	-0.55
NMe ₂	-0.07	-0.16	-0.27	0.17	-0.44	-0.61
Ph		0.09	0.01	0.12	-0.11	-1.01
OPh		0.23	-0.02	0.40	-0.42	-0.55
<i>t</i> -Bu		-0.09	-0.19	-0.01	-0.18	-2.78
Et		-0.08	-0.15	-0.01	-0.14	-1.31

^a Values of σ_m are those recommended in Exner compilation, when possible (ref 23). Values of E_s are Taft-Kutter-Hansch steric parameters with the reference point shifted to H, as in ref 9a. All other parameters have been taken from Charton's recent compilation (ref 13). ^b Value for planar nitro group.

values of Hammett substituent constants²⁰ is significant ($r = 0.980$, 6 points), but it is better ($r = 0.990$) if σ_p° values are used (see Figure 1). This is to be expected, in view of the absence of conjugation in the aryl anion. Among the different "unbiased" or "normal" σ_p° available, the set of Taft²¹ gives the best correlation ($r = 0.993$), but, for the sake of completeness and self-consistency, throughout the paper we use exclusively the parameters in Table II.

Eaborn and collaborators calculated the deprotonation energies of ortho, meta, and para monosubstituted benzenes, at the ab initio STO-3G level with fixed standard geometries.²² From these energies, the energy balances ΔE for the isodesmic process of eq 5 were calculated, the published values being shown in the last three columns of Table I.



Eaborn et al. found poor correlations between the calculated ΔE and the experimental $\log k_{rel}$ for the meta and para compounds in reactions B and C; they attributed the lack of good correlation to limitations or errors in the MO calculations. However, we have obtained a very significant regression ($r = 0.9990$, 4 points) between the $\log(k_{rel})_p$ in reaction A and ΔE_p , as illustrated in Figure 2. If, for comparison purposes, Br (which has virtually the same reactivity as Cl) and I (for which no ΔE value is available) are excluded from the plot of Figure 1, it becomes considerably less significant ($r = 0.992$, 4 points) than the one of Figure 2. Hence, ΔE shows up as the best available explanatory variable to account for the reactivity of para compounds in reaction A. Thus, we think that the main source of scatter in the Eaborn plots is not in ΔE but in the kinetic data.

Although the reactivity of para compounds in reaction A apparently correlates better with ΔE_p than with σ_p° , the lack of calculated energies for many substituted benzenes obliges us to carry the analysis of electronic effects in terms of σ_p° . This analysis is shown in Table III and will be used

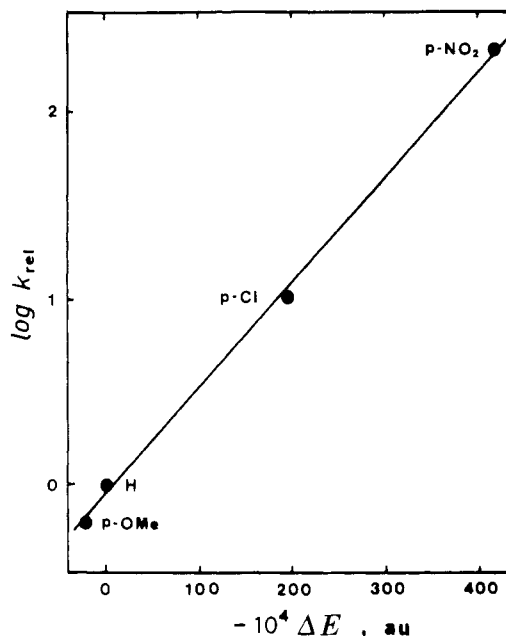


Figure 2. Plot of $\log(k_{rel})_p$ of reaction A vs. ab initio calculated energy for the isodesmic process of eq 5.

later for comparison of the ρ values.

Ortho Parameters from Calculated Energies. The remarkably good correlation of Figure 2 and the fact that ΔE values do not refer to any particular solvent (like the Hammett substituent constants) make us consider ΔE_o as the best available parameters to factor ordinary electronic effects at the ortho position in reactions via aryl anion intermediates. To put ΔE_o on the same scale as $\sigma_{m,p}$, the values of the former have been converted according to eq 6. The conversion factor is the slope of the regression (r

$$\sigma_o^\circ = -198\Delta E_o \quad (6)$$

= 0.96, 17 points, not shown) of $\sigma_{m,p}$ against $\Delta E_{m,p}$; we have preferred to use this slope instead of the unrestricted one (-203) in order to assure that $\sigma_o^\circ = 0.00$ for H. The obtained σ_o° values are shown in the second column of Table II.

Energy values at the STO-3G level for the isodesmic process of eq 5 with X = Br and I are not available, so we are forced to estimate ΔE_o values for these two substituents. Given that all electronic substituent parameters for Cl and Br are equal (see Table II), it is reasonable to assume $\Delta E_o(\text{Br}) = \Delta E_o(\text{Cl})$, and then $\sigma_o^\circ(\text{Br}) = \sigma_o^\circ(\text{Cl})$. The value of $\Delta E_o(\text{I})$ has been estimated in a dual-substituent parameter analysis of the type of eq 7 ($Q \equiv \Delta E_o$)^{23,24} and is the value predicted by the regression for the known values of $\sigma_R(\text{I})$ and $\sigma_F(\text{I})$.

$$Q = \rho_R\sigma_R + \rho_F\sigma_F + c \quad (7)$$

Correlation Analysis of the Ortho Effect. With the kinetic data of Table I, multilinear analyses of the type of eq 4 have been carried out in parallel, first with the original assumption of $\sigma_o^\circ \equiv \sigma_p^\circ$ (method I) and then with use of the semiempirical σ_o° parameters of Table II (method II). The results of the analyses, shown in Table IV, indicate that the two methods provide different interpretations of the ortho effect.

According to method I, the steric contributions to the ortho effect in reactions A and B are negligible. On the

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Table III. One-Parameter Analysis (eq 3) of the Reactions in Scheme I (Only Meta and Para Compounds)^a

reactn	T, °C	ρ	c	n	s	r
A	125.0	2.86 ^b (± 0.22)	0.21 (± 0.08)	6	0.156	0.990
B	40.0	5.59 (± 0.21)	0.19 (± 0.07)	18	0.263	0.990
C	-33.3	7.09 (± 0.63)	0.47 (± 0.15)	16	0.570	0.95

^an, number of points; s, standard deviation of the estimate; r, correlation coefficient. Uncertainty of parameters expressed as standard errors. ^bValues of ρ at other temperatures, from extrapolated values of rate constants: 3.92 \pm 0.22 (40.0 °C); 5.45 \pm 0.25 (-33.3 °C).

Table IV. Comparison between the Analysis of the Ortho Effect in the Reactions of Scheme I by Two Methods: the Current One (Method I, $\sigma^{\circ}_o \equiv \sigma^{\circ}_p$) and the Here Advocated One (Method II, Semiempirical σ°_o)

reactn	method	ρ	f	δ	c	n	s	r	F ^a	SL, ^b %
A	I	3.05 (± 0.21)	5.35 (± 0.22)	ns	0.15 (± 0.08)	10	0.17	0.997	583	
A	II	2.98 (± 0.21)	ns	-1.25 (± 0.08)	0.17 (± 0.08)	10	0.15	0.998	724	
B	I	4.74 (± 0.36)	3.87 (± 0.57)	ns	0.41 (± 0.13)	24	0.53	0.963	135	
B	II	5.23 (± 0.11)	2.86 (± 0.75)	0.57 (± 0.25)	0.29 (± 0.11)	24	0.46	0.976	134	98
C	I	6.44 (± 0.57)	10.0 (± 1.1)	0.60 (± 0.30)	0.57 (± 0.15)	21	0.61	0.968	85	94
C	II	7.39 (± 0.62)	7.69 (± 1.09)	0.55 (± 0.28)	0.41 (± 0.14)	21	0.58	0.972	95	93

^aF value for the significance of the regression. ^bSignificance Level (in %) for the introduction to the third explanatory variable (ns when less than 90%).²⁵

contrary, according to method II the steric contribution is more important than the proximity electronic one in reaction A (the latter being negligible), and it is significant in reaction B. For reaction C both methods indicate similar contributions of steric effect, but method I gives a much higher proximity electronic effect and, consequently, a much lower ordinary electronic effect.

For the three reactions, method II gives better correlations than method I from the statistical point of view (compare the statistics of Table IV). Besides, ρ values obtained by method II are much closer to the corresponding values in Table III. The result of the analysis of reaction A by method II is depicted in Figure 3.

Discussion

Superiority of Semiempirical Ortho Parameters.

The better statistical significance of the correlation analysis when semiempirical ortho parameters are used has only relative importance; what should be stressed is that these parameters provide a better analysis from the chemical point of view, giving ρ values closer to the ρ values for meta and para compounds. This success stems from a more realistic blending of polar and resonance components in the semiempirical σ°_o than in σ°_p , for the ortho position.

Comparing the different values of ρ for meta- and para-substituted compounds for the three reactions at the same temperature (Table III and its footnotes), one sees that the ordinary polar effect is smaller in reaction A than in the other two. This is understandable given the higher polarity of the solvent in reaction A and the presence of the two extra nitro groups, which surely withdraw part of the negative charge of the aryl anion.

According to the output of method I, the proximity electronic effect is very important in all three reactions; to reaction A corresponds the highest value, relative to the ordinary electronic effect ($f/\rho = 1.75$). The output of method II is quite different: the relative importance of the proximity electronic effect is lowest for reaction A (f/ρ negligible), considerably larger for reaction B ($f/\rho = 0.55$), and the largest for reaction C ($f/\rho = 1.0$). According to our qualitative theoretical interpretation of the proximity electronic effect (see below), this should be smaller the higher the dielectric constant of the solvent, other factors being equal. This view is coherent with the results of the analysis by method II (the solvents are H₂O, Me₂SO, NH₃, respectively) but not with those by method I.

The value $\delta = -1.25$ given by method II for reaction A means an important steric acceleration, which is reasonable

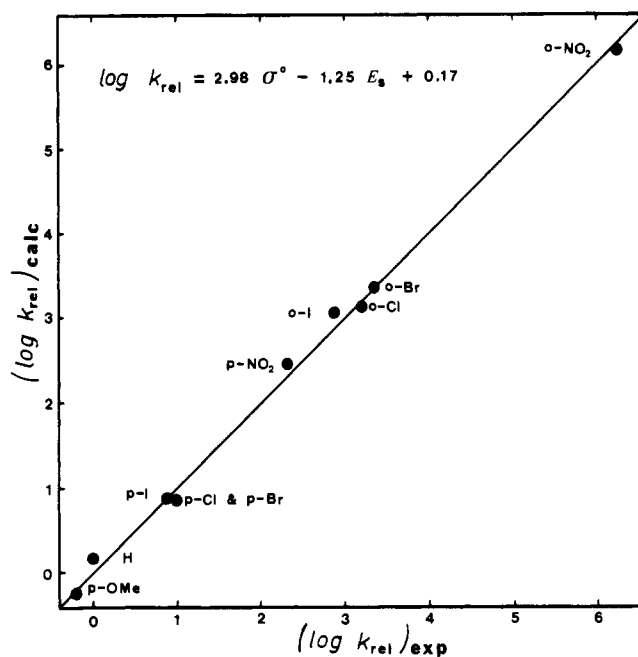


Figure 3. Plot of calculated vs. experimental values of $\log(k_{rel})_{o,p}$, corresponding to the analysis of the ortho effect in reaction A by the method here advocated.

considering that the carboxylate group with its solvation sphere should be bulky, and that there should be a considerable release of steric compression in the transition state. However, according to the original model of Fujita and Nishioka (method I), the reaction does not show any steric effect at all. The small value of δ in reaction C is understandable; the steric requirements for transfer of a proton to the small base NH₂⁻ should be minor.

In all the correlations of Table IV we have used the popular Taft-Kutter-Hansch E_s steric parameters, following the original practice of Fujita and Nishioka. However, the question of which steric parameters are the best for correlation analysis is not settled and has been the subject of recent reviews.²⁶ It is illustrative that an author reached contrary conclusions in two consecutive papers.⁷

(25) See, for instance: Shorter, J. "Correlation Analysis in Organic Chemistry: An Introduction to LFER"; Clarendon Press: Oxford, 1973; Appendix.

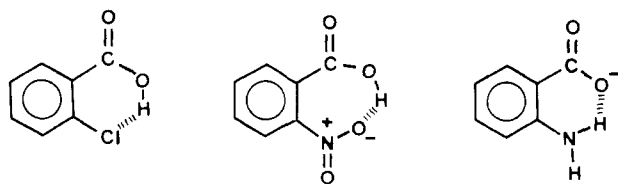
(26) (a) Fujita, T.; Iwamura, H. *Top. Curr. Chem.* 1983, 114, 119-157. (b) Gallo, R. *Prog. Phys. Org. Chem.* 1983, 14, 115-163.

Research in this field will undoubtedly assist the analysis of the ortho effect.

The signs and absolute values of the different slopes in correlations of the type of eq 4 are potentially a rich source of mechanistic information (as the values of ρ are already). Steric effects are expected to depend strongly on changes in solvation within the reaction site, and proximity electronic effects will probably be interpreted in terms of charge change, charge distance, and solvent polarity. But before sound generalizations can be reached, this kind of analysis should be applied to many reactions with well-established mechanisms.

Unfortunately, little can be concluded from analysis of the three reactions of Scheme I, given that reaction A is the only one to which one can confidently assign the simple mechanism of rate-limiting formation of an aryl anion.¹ In reaction B the mechanistic information available does not exclude the possibility of a preequilibrium in which the base (OH⁻) adds to the silicon atom, before rate-limiting formation of the aryl anion.²⁷ Related to reaction C, the H/D exchange of substituted benzenes catalyzed by MeONa in MeOH has given indicators of an important contribution of internal return, which would give a second-order rate constant of the form $k_{\text{obsd}} = k_1 k_2 / (k_{-1} + k_2)$ or even $k_{\text{obsd}} = K_1 k_2^{17f,g}$. This internal return could be important also in ammonia (reaction C), thus blurring the meaning of k_{obsd} in relation to the rate coefficient for the formation of the aryl anion (k_2).

Failure of Gas-Phase Acidities To Estimate Ortho Parameters. Gas-phase acidities of meta- and para-substituted phenols and benzoic acids have been measured, and their relation to solution acidities has been fully discussed.^{28,29} The gas-phase acidities of some ortho-substituted phenols have been measured as well, but not in enough number and variety to allow the evaluation of ortho parameters.²⁸ However, McMahan and Kebarle have measured the gas-phase acidities of ortho-substituted benzoic acids, the substituents being NO₂, F, Cl, CH₃, OCH₃, OH and NH₂.²⁹ They found a good correlation between relative acidities ($\Delta G_{\text{m,p}}$) and $\sigma_{\text{m,p}}$ parameters. Thus one could think of using ΔG_0 to estimate σ_p parameters (empirical, not semiempirical, because no calculation would be involved). We have done this estimation, but the resulting ortho parameters do not represent the ordinary electronic effect only and they are not suited for the use in correlation analysis. The reason is the presence of strong hydrogen-bond interactions, either in the acid or in the anion, like those shown in structures I–III.²⁹



Hydrogen-bond interactions of this type are also expected in ortho-substituted phenols and amines and will be reproduced—at least in part—by MO calculations. Therefore, we think that deprotonation of phenols, anilinium ions, or benzoic acids are not appropriate isodesmic processes to estimate ortho parameters. As precise values for the gas-phase acidities of substituted benzenes and

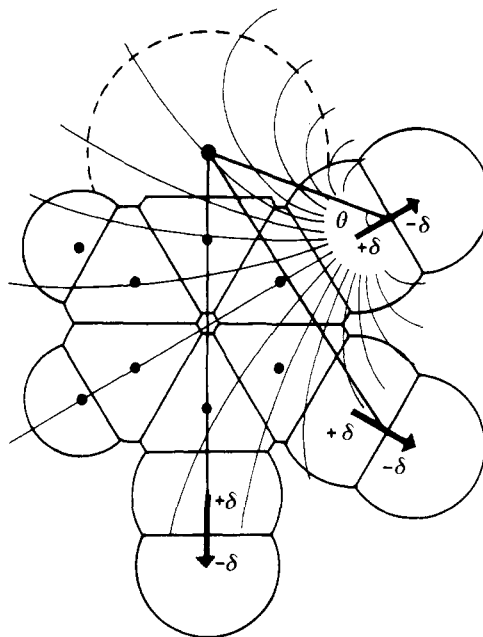


Figure 4. "Space-filling" model (spheres of 80% of van der Waals radii) of a general *o,m,p*-tricyano-substituted-benzene. Some symmetrical lines of force of the ortho dipole have been drawn.

toluenes are not to be expected in the near future, it is unlikely that suitable ortho parameters could be estimated from gas-phase acidities.

Qualitative Interpretation of the Ordinary and the Proximity Electronic Effects. As a visual example of a substituted benzene, a "space filling" model of a tricyano-substituted benzene is shown in Figure 4. In the model bond lengths and angles are standard, and spheres of 80% of van der Waals radii are considered to represent the "size" of the atoms. An arbitrary reaction site, of 2-Å radius and distance of 1.5 Å from C-IPSO, is also drawn (dashed line).

Recent findings have established that the traditional "inductive effect" is mostly a field effect,³⁰ and a consequent change in terminology and symbols is being adopted.¹⁴ MO calculations on fluorobutane, for instance, shows that the inductive effect, if it really operates, will affect only the C atom bearing the F and the next neighbor, but not further away.³¹ This means that, with the possible exception of aryl anions (see below) and aryl cations, the contribution of the inductive effect to the ortho effect will be negligible in comparison with that of the field effect. Therefore, only the latter needs to be considered.

Attempts to rationalize field effects have been mainly based on the electrostatic model of Kirkwood and Westheimer,³² according to which the energy interaction between a charge and the dipole of a substituent should be proportional to $\cos \theta / r^2 D$, r being the distance to the center of the dipole, θ the angle formed by r and the vector of the dipole, and D the dielectric constant of the medium. The application of this relation to the ortho, meta, and para cyano substituents of Figure 4 (for a constant D and assuming that the center of the dipole is the middle of the C≡N bond and that the charge is located at the center of the reaction site) gives the relative values 2.4:1.2:1.0. These figures qualitatively illustrate the commonly accepted idea that field effects are of similar intensity for meta and para

(27) Eaborn, C.; Seconi, G. *J. Chem. Soc., Perkin Trans. 2* 1979, 203.

(28) Fujio, M.; McIver, R. T.; Taft, R. W. *J. Am. Chem. Soc.* 1981, 103, 4017–4029.

(29) McMahan, T. B.; Kebarle, P. *J. Am. Chem. Soc.* 1977, 99, 2222–2230.

(30) See, for instance: Reynolds, W. F. *J. Chem. Soc., Perkin Trans. 2* 1980, 985–992.

(31) Topsom, R. D. *Acc. Chem. Res.* 1983, 16, 292–298.

(32) For a brief introduction, see ref 33, pp 29–37.

substituents and larger for ortho substituents. Problems with this electrostatic model arise when regions of different dielectric constant are considered.

According to electrostatics theory, the lines of force of an electric field concentrate more in zones of space with a lower dielectric constant. The D value for the interior of the benzene nucleus should be small (about 2.3, the value for bulk benzene), whereas the D value of the solvent will change according to its polarity (up to 78, the D of bulk water). A given field interaction will be greatest for vacuum ($D = 1.00$ by definition). It is known that, in going from aqueous solution to the gas phase, the increments of the total electronic effect (field + resonance) are large (a factor of 10.6 for the acidity of benzoic acids and 6.8 for phenols).²⁹ We have found that for the energy calculation of the isodesmic processes of Scheme II they are still larger.³⁴ But the fact that the same Hammett parameters generally account for the changes in reactivity in very different reactions, in different solvents, in the gas phase, and in MO calculations, strongly suggests that the transmission of resonance and field effects from meta and para positions to the reaction site is a peculiar property of the benzene nucleus, i.e., it is a peculiar *through-the-nucleus* interaction.³⁵ The estimation of electronic ortho parameters from calculated energies only assumes that the same peculiarity exists for the ortho position; this seems much more reasonable than the existence of a coincidence between ortho and para electronic effects.

However, whereas for meta and para substituents the resonance and field interactions through-the-nucleus constitute the whole interaction, for ortho substituents an extra field interaction *through-the-solvent* is expected. To illustrate qualitatively this point, some symmetrical lines of force for the ortho dipole have been drawn in Figure 4. This extra field interaction, that we identify with the proximity electronic effect, should be smaller the higher the dielectric constant of the solvent, other factors being equal. In an ortho-substituted aryl anion (or in a transition state of similar structure), the negative charge is mainly on the C-*ipso*; therefore the field effect should take place necessarily through the nucleus. This factor and the high polarity of the solvent (H₂O) justify our conclusion that the proximity electronic effect in reaction A is negligible.

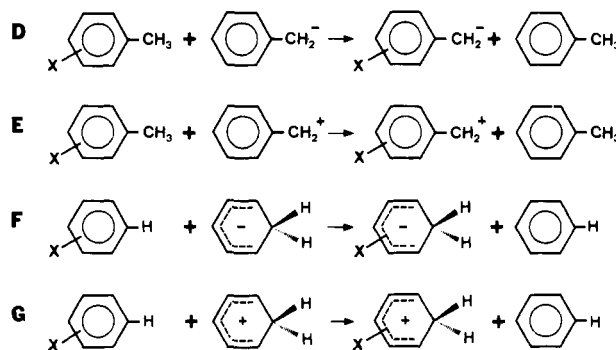
General Approach To Estimate Ortho Parameters of Wide Applicability. A dual-substituent parameter analysis (eq 7) of the σ° values in Table II gives a blending ratio $\rho_F/\rho_R = 2.0$, much higher than that corresponding to σ°_p (1.0 by definition). Actually, a blending ratio of 2.0 seems too high for the ortho position in respect to common reactions of benzene compounds, suggesting that the σ° values of Table II should be applicable only to reactions via aryl anion intermediates. This high value is understandable considering two special circumstances that differentiate the aryl anion from other benzene intermediates. First, that the negative charge is localized in the σ framework and extraordinarily concentrated on the ipso carbon atom (σ charge of -0.7 , according to MO calculations²²); second, that the ipso carbon atom is only one bond removed from the carbon bearing the substituent. Therefore the ipso carbon still can experience some inductive effect (but it is probably negligible at the benzylic position). Thus, it seems desirable to estimate σ_o for more common reactions.

(33) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, 1975; pp 58-65.

(34) Segura, P.; Geijo, F.; Olivella, S.; Sole, A., to be published.

(35) In Leffler-Grunwald terms (ref 39), at meta and para positions, resonance and field effects are two interaction mechanisms whose relative importance is constant.

Scheme II. Isodesmic Processes Recommended To Estimate Semiempirical Ortho-Substituent Parameters for Common Reactions of Benzene Compounds



Considering the structures of the typical intermediates in the most common reactions of benzene compounds, and the requirement of steric tension as low as possible in the substrates to be calculated, we deem the four isodesmic processes of Scheme II to be the most suitable to obtain ortho parameters of wide applicability. To date, no MO energies for any of the ortho-substituted derivatives of Scheme II have been published; however, the situation is different for meta and para series. In 1976 Streitwieser and Hehre found a correlation between σ^+ parameters and ΔE calculated for isodesmic process G.³⁶ Recently, Pross, Radom, and Taft have calculated the energy data necessary for the meta and para series of isodesmic process D.³⁷ All these calculations were at the STO-3G level, with non-optimized standard geometries, and for one or two fixed conformations, although several are possible. However, geometry optimization should be a crucial factor for ortho substrates. We have calculated the energies of isodesmic processes D and E, including the ortho series, at the STO-3G level, with geometries previously optimized at the MNDO level (MNDO//STO-3G calculations). This has allowed us to estimate a set of semiempirical σ_o parameters, different from the σ°_o of Table II and with a more reasonable blending ratio. A detailed estimation of ortho parameters for common reactions of benzene compounds, both from semiempirical and ab initio MO calculations, will be the subject of a forthcoming publication.³⁴

The fact that ab initio MO calculation at STO-3G level reproduce successfully the experimental heats of isodesmic processes has been known for a long time.³⁸ However, although both the Leffler-Grunwald³⁹ and Hine³³ approaches to the Hammett equation emphasize the energetic (free energy) nature of σ parameters, theoretical interpretation of substituent effects from MO calculations has been done mainly in terms of charge population or perturbation MO theory, not in terms of energy.^{31,40,41} Topsom provides a recent example: In order to define his

(36) McKelvey, J. M.; Alexandratos, S.; Streitwieser, A.; Abboud, J.-L. M.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 244-246.

(37) (a) Kemister, G.; Pross, A.; Radom, L.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 1056-1059. (b) Kemister, G.; Pross, A.; Radom, L. *J. Comput. Chem.* **1981**, *2*, 470-477.

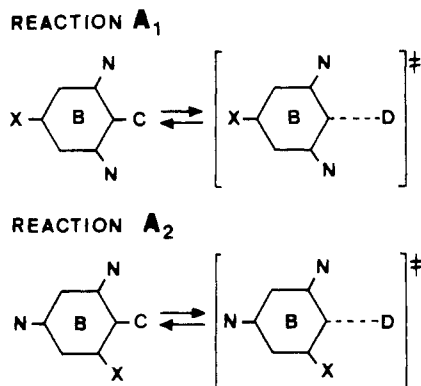
(38) (a) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. (b) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 5935. (c) Radom, L. *J. Chem. Soc., Chem. Commun.* **1974**, 403-404.

(39) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; Chapter 7.

(40) See, for example, the following reviews: (a) Pross, A.; Radom, L. *Prog. Phys. Org. Chem.* **1980**, *13*, 1-61. (b) Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 1-20. (c) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159-187.

(41) Marriott, S.; Reynolds, W. F.; Taft, R. W.; Topsom, R. D. *J. Org. Chem.* **1984**, *49*, 959-965.

Scheme III. Schematic Representation of the Activation Process in Reaction Series A₁ and A₂, Formally Treated as Equilibria: N = NO₂; B = Benzene Nucleus; C = CO₂; D = CO₂; X = Substituent



theoretical (not semiempirical) field effect parameters, he considered both an energy approach and a charge density one; although at the beginning he chose to mix both approaches taking average values,³¹ he finally decided in favor of the charge density approach.⁴² The method to estimate semiempirical σ_o parameters that we advocate goes back to the fundamental energetic nature of the σ parameters.

A good correlation between $(\Delta E)_{m,p}$ —calculated enthalpies— and $\sigma_{m,p}$ —experimental Gibbs energies—is consistent with the existence of an isokinetic relationship for the meta and para reactions of a reaction series. The same relationship should hold for the hypothetical ordinary electronic effect in the ortho reactions; therefore, it seems reasonable to evaluate σ_o from calculated $(\Delta E)_o$. In any case, the ultimate justification of the assumptions involved will be the future usefulness of this approach.

Conclusion

The assumption that the ordinary electronic effect at the ortho position can be represented satisfactorily by the corresponding para parameter should be abandoned, because it leads to a misunderstanding of the ortho effect, typically, to an underestimation of the steric contribution. At the moment, the use of semiempirical ortho parameters like those now proposed seems the best alternative solution. The general procedure to estimate them can be summarized as follows: (Step 1) For a given reaction, take the best available meta and para calculated energy data for the most suitable isodesmic process and correlate them with the meta and para experimental substituent parameters that best describe the reactivity. (Step 2) With the slope of that correlation, estimate ortho parameters from the calculated ortho energies. (Step 3) Revise and update these semiempirical ortho parameters when a better isodesmic process is discovered or better energy calculations are available.⁴³

Acknowledgment. I thank Prof. Joseph F. Bunnett and Prof. Josep Castells for the reading of the manuscript and for their comments and suggestions and also the United States–Spain Joint Committee for Scientific and Technological Cooperation for a fellowship.

Appendix

Theoretical Interpretation of Separation of Effects in Reactions A₁ and A₂. To interpret the separation of

substituent effects in reactions A₁ and A₂ and to justify that the $\log(k_{rel})_o$ and $\log(k_{rel})_p$ have been combined in a single correlation of the type of eq 4 (not obvious because of the presence of the two extra nitro groups), we will develop an approach parallel to the one of Hine.³³ This approach is based on the assumption that the Gibbs energy contents of the species involved may be expressed as the sums of the contributions of the different structural components (groups, group–benzene nucleus, and group–group). The treatment for ortho compounds will be generalized to include both ordinary and proximity electronic effects. The notation of Scheme III will be used.

Reaction A₁. The Gibbs energy contents of the transition state may be expressed as in eq 8. In this equation, $G^*_{pX} = G^B + G^X + 2G^N + G^D + G^{XB} + 2G^{NB} + G^{DB} + (G^{XD/B})_p + 2(G^{XN/B})_m + (G^{NN/B})_m + 2(G^{ND/B})_o + 2(G^{ND/s})_o$ (8)

term G^X represents the contribution of group X; term G^{XB} represents the contribution of the interaction between the group X and the benzene nucleus B; term $(G^{XD/B})_p$ represents the contribution of the interaction between X and D through the nucleus B in a para relative position; and term $(G^{ND/s})_o$ represents the contribution of the interaction between groups N and D through the solvent (s), that we assume is significant only for the relative ortho position.

An equation similar to eq 8, only replacing C by D in every place it appears, can be written for the Gibbs energy contents of the initial state. When both energies are subtracted to give the Gibbs energy of activation, many terms cancel and eq 9 is obtained.

$$\Delta G^*_{pX} = (G^{DB} - G^{CB}) + [(G^{XD/B})_p - (G^{XC/B})_p] + 2[(G^{ND/B})_o - (G^{NC/B})_o] + 2[(G^{ND/s})_o - (G^{NC/s})_o] \quad (9)$$

An equation similar to eq 9, only with X replaced by H in every place it appears, can be written for the Gibbs energy of activation of the reaction with the unsubstituted substrate. When relative rate constants are considered, most of the terms cancel out leaving only those in eq 10.

$$\log(k_{rel})_p = \log(k_{pX}/k_{pH}) = (-2.3RT)^{-1}(\Delta G^*_{pX} - \Delta G^*_{pH}) = (-2.3RT)^{-1}\{[(G^{XD/B})_p - (G^{HD/B})_p] - [(G^{XC/B})_p - (G^{HC/B})_p]\} = (-2.3RT)^{-1}[\delta(G^{XD/B})_p - \delta(G^{XC/B})_p] \quad (10)$$

Equation 10 shows that $\log(k_{rel})_p$ accounts only for the differential effect that the change of the para-substituent (expressed as a Leffler–Grunwald operator δ) has on the interaction between the reaction site and the substituent through the benzene nucleus. The effects of the two extra nitro groups cancel out. Every term of that interaction can be expressed as a product of a reaction site parameter σ^D , a substituent parameter σ_p^X , and a proportionality factor characteristic of the nucleus ρ^B , as shown in eq 11

$$(G^{XD/B})_p = -2.3RT\rho^B\sigma_p^X\sigma^D \quad (11)$$

for one interaction term. Making the appropriate assignments in eq 10, converts it into eq 12, which justifies the existence of a single-substituent-parameter correlation in reaction A₁.

$$\log(k_{rel})_p = \rho^B(\sigma^D - \sigma^C)(\sigma_p^X - \sigma_p^H) \quad (12)$$

Reaction A₂. The Gibbs energy contents of the transition state may be expressed in the form of eq 13.

$$G^*_{oX} = G^B + G^X + 2G^N + G^D + G^{XB} + 2G^{NB} + G^{DB} + (G^{XD/B})_o + 2(G^{XN/B})_m + (G^{NN/B})_m + (G^{ND/B})_p + (G^{ND/B})_o + (G^{XD/s})_o + (G^{ND/s})_o \quad (13)$$

(42) Marriott, S.; Topsom, R. D. *J. Am. Chem. Soc.* 1984, 106, 7–10.

(43) At the moment, because of the size of the involved substrates, we are probably limited to the STO-3G level (ref 31).

From consideration of the log $(k_{rel})_o$, eq 14 is obtained.

$$\log (k_{rel})_o = (-2.3RT)^{-1} \{ [\delta(G^{XD/B})_o - \delta(G^{XC/B})_o] + [\delta(G^{XD/S})_o - \delta(G^{XC/S})_o] \} \quad (14)$$

On the right side of eq 14 the first term has the same nature as the one in eq 10 and corresponds to what is called the ordinary electronic effect at the ortho position. The second term represents the proximity electronic effect that we factor as a sum of a through-the-solvent field interaction and a steric interaction, according to eq 15. Making

$$(G^{XD/S})_o = -2.3RT(\lambda^{Bf} X_f^{fD} + \delta^{Be} X_e^{eD}) \quad (15)$$

the necessary substitutions and cancelations, one obtains eq 16, which justifies theoretically the separation of effects

$$\log (k_{rel})_{o,p} = \rho^B(\sigma^D - \sigma^C)(\sigma^X - \sigma^H)_{o,p} + \lambda^B(f^D - f^C)(f^X - f^H)_o + \delta^B(e^D - e^C)(e^X - e^H)_o \quad (16)$$

indicated in eq 2, i.e., the legitimacy of the Fujita-Nishioka separation of effects. Considering eq 10 and 14, we may properly mix the log k_{rel} data from reactions A₁ and A₂ in a single correlation (eq 4) if we assume that the ortho and para interactions between X and the reaction site through the nucleus B represent the same kind of phenomenon (ordinary electronic effect). This assumption would be quite reasonable if the two extra nitro groups were absent, but it is still reasonable because the presence of the two nitro groups in the given positions should modify the electronic structure of the nucleus in very similar ways.

Rates of Bromination of Dimethyl Fumarate and of Dimethyl Acetylenedicarboxylate¹

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Received September 7, 1984

Rates of bromination of dimethyl fumarate and of dimethyl acetylenedicarboxylate were determined in 50% aqueous acetic acid in the presence of varying amounts of sodium bromide. In the presence of bromide ions both substrates are believed to react by the termolecular Ad_E3 mechanism, and the acetylenic substrate reacts faster than the olefin. The acetylene also reacts faster in the reaction which involves a bimolecular attack by bromine (Ad_E2). Usually olefins react considerably faster than acetylenes in halogenation, and possible reasons for the reversal of the relative rates observed here are discussed.

The problem of the relative reactivities of alkenes and alkynes in various electrophilic addition reactions (k_o/k_a) has been well recognized in recent years and has been critically documented and discussed in a recent review article.^{3,4} Briefly, while bond energy data⁵ and the greater electron density in alkynes than alkenes would suggest a greater reactivity for alkynes, the experimental data do not usually bear this out. There are those reactions, typified by acid-catalyzed hydration, where double and triple bonds are about equally reactive, and those like halogenation, where simple olefins react many thousand times faster than acetylenes. These large differences in bromination and chlorination have usually been ascribed to the difference in energy of the cationic intermediates involved.^{3,4,6}

What has been less often discussed is the puzzling effect of substituents on the relative rates of halogenation of double and triple bonds. *trans*-3-Hexene reacts 3.4×10^5 times faster than 3-hexyne in bromination in acetic acid.⁷ An electron-attracting phenyl group reduces the ratio:

trans-1-phenylpropene reacts 5000 times faster than phenylmethylacetylene and styrene 2600 times faster than phenylacetylene. A second phenyl group in the pair stilbene/tolan reduces k_o/k_a to about 250.⁸ Introduction of the stronger electron-attracting carbomethoxy group reduces the ratio further, and methyl *trans*-cinnamate is only 27 times more reactive than methyl phenylpropionate.^{9,10} We have now extended the comparison to the pair dimethyl fumarate and dimethyl acetylenedicarboxylate.

Results and Discussion

The two esters were brominated under identical conditions in 50% aqueous acetic acid (by volume) in the presence of varying amounts of sodium bromide, as was done previously.⁹ Under these conditions the rate expression is $-d(\text{Br}_2)_T/dt = k_{\text{obsd}}(\text{Br}_2)_T(A)$, where $(\text{Br}_2)_T$ refers to the total titratable bromine and A to the unsaturated substrate. In the presence of bromide ion, the total rate of bromination can then be expressed by eq 1.^{9,11} In this

$$-d(\text{Br}_2)_T/dt = k_2(\text{Br}_2)(A) + k_3(\text{Br}_2)(\text{Br}^-)(A) \quad (1)$$

equation the first term represents a bimolecular reaction of free bromine with the substrate, and the second term a termolecular, bromide ion assisted process. This term,

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(9) (a) DeYoung, S.; Ehrlich, S.; Berliner, E. *J. Am. Chem. Soc.* 1977, 99, 290. (b) Ehrlich, S.; Berliner, E. *Ibid.* 1978, 100, 1525. (c) DeYoung, S.; Berliner, E. *J. Org. Chem.* 1979, 44, 1088.

(10) A ratio of 3 has been reported for the corresponding acids in bromination in acetic acid and of 2.5 in methanol. (a) Robertson, P. W. *Rev. Pure Appl. Chem.* 1957, 7, 155. (b) Schmid, G. H.; Modro, A.; Yates, K. *J. Org. Chem.* 1977, 42, 2021.

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(1) Kinetics of Halogenation of Olefins and Acetylenes. 7. For part 6 in this series, see ref 9c.

(2) Taken in part from the Senior Honors Theses of S. A. Wolf and S. Ganguly, Bryn Mawr College, May 1980 and 1984.

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(4) See also: (a) de la Mare, P. B. D.; Bolton, R. In "Electrophilic Additions to Unsaturated Systems", 2nd ed.; Elsevier: Amsterdam, 1982, Chapter 9. (b) Schmid, G. H. In "The Chemistry of the Carbon-Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1973; Part 1, Chapter 8.

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