mg (1.6 mmol) of α-bromobenzyl phenyl sulfone with 3.0 g of triphenylphosphine in 15 ml of 5% methanol in benzene at reflux for 20 hr gave *ca.* 15% reduction (benzyl phenyl sulfone) and 80% recovered starting material. Essentially the same result was obtained using 5% acetic acid in benzene as the solvent.

This same reaction with benzyl α-bromobenzyl sulfone (500 mg) and 3.0 g of triphenylphosphine gave 80% reduction after 30 hr in 20 ml of 5% methanol in benzene at reflux.

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Semiempirical Models for Substituent Effects in Electrophilic Aromatic Substitution and Side-Chain Reactions

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Abstract: Semiempirical substituent effect models are formulated which successfully predict relative rates of reaction for a wide variety of substituted aromatic systems, in both electrophilic aromatic substitution and electrophilic side-chain reactions. The semiempirical equations are based on the separation of effects into field and resonance terms. The approach treats the effects of substituents as perturbations affecting the reactivity of parent aromatic systems through the mechanisms of substituent interaction with the charge developed in the transition state. The approach is evaluated on the basis of success in handling the available data for protodetritiation and solvolysis in substituted aromatic systems. New quantitative data are reported for the solvolysis of a series of substituted 1-(2-benzo[*b*]thienyl)ethyl *p*-nitrobenzoates.

The modification of the Hammett equation introduced by Brown and Okamoto by the definition of σ^+ constants[2] has proven remarkably useful for the treatment of substituent effects in benzene for reactions in which a positive charge developed in the transition state is stabilized by delocalization into the aromatic ring. However, in extending the Hammett equation to other aromatic systems, an approach based on empirically defined constants would necessitate establishing a very large number of substituent constants to cover all possible positional orientations of substituent site and reaction center in every aromatic nucleus. Capabilities for prediction of reaction rates in new systems are obviously limited if restricted to dependence upon previously determined, purely empirical σ^+ constants. Furthermore, such a purely empirical approach contributes little to the understanding of the relationships underlying the effects of substituents.

On the other hand, the strictly nonempirical approach of calculating energy differences between ground states and transition states for each substituted molecule by quantum-mechanical means also has limitations of practicality. Approximate quantum-mechanical methods have shown some success in treating the reactivity of substituted benzenes,[3,4] but in one sense the totally quantum-mechanical approach is similar to the totally empirical approach: independent operations must be performed for each situation, *i.e.*, costly calculations are necessary for every substituent in each arrangement of substituent site and reaction center in every aromatic system considered. Neither the quantum-mechanical approach nor the purely empirical method takes advantage of the expected similarities in the effect of substituents on a variety of aromatic systems.

We wish to report in this paper a semiempirical approach for the quantitative correlation and prediction of aromatic substituent effects for electrophilic substitution and solvolysis reactions. This semiempirical approach treats the effects of substituents as perturbations affecting the reactivity of the parent aromatic systems. By identifying the mechanisms of substituent perturbations and by referring to observed effects in a basis system (benzene), mathematical models are developed to estimate the perturbations for other aromatic molecules. These semiempirical models combine fundamental theoretical concepts with empirically derived parameters to produce a method more practical than either purely empirical or purely theoretical treatments. The approach will be evaluated on the basis of success in handling the available data for protodetritiation and solvolysis in substituted aromatic systems and will be compared with previously used methods.

In using the modified Hammett equation for the correlation

$$\log k/k_0 = \sigma^+\rho \qquad (1)$$

of relative rates of electrophilic reactions for substituted benzenes, it is necessary to know either σ_p^+ or σ_m^+ constants for the substituents involved, depending upon the site of substitution relative to the reaction center. To use the Hammett equation to predict relative rates, it is necessary to know both the σ^+ constants and the ρ value for the reaction being considered. Clearly, in extending the Hammett equation to other aromatic systems, the desirable approach is one which

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[1] National Institutes of Health Predoctoral Fellow, 1970–date (GM-49,851).

[2] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

[3] A. Streitwieser, Jr., H. A. Hammond, R. J. Jagow, R. M. Williams, R. G. Jesaitis, C. J. Chang, and R. Wolf, *J. Amer. Chem. Soc.*, **92**, 5141 (1970).

[4] G. R. Howe, *J. Chem. Soc. B*, 984 (1971).

will provide for the calculation of the appropriate substituent constants for any position in any aromatic molecule, and for maximum predictive value the substituent constants should be properly scaled so that the ρ value for a reaction as determined for benzene is applicable to all aromatic systems undergoing the same reaction. Dewar and Grisdale formulated such an approach for the calculation of the effect of substituents on the dissociation of aromatic carboxylic acids and for other processes normally correlated with σ_p and σ_m constants in the benzene series.[5] Their substituent effect model was based on assumed field and mesomeric mechanisms for transmission of the effects in aromatic molecules.[6] A later, modified version also was formulated by Dewar, Golden, and Harris.[7] We report in this paper the analogous formulation of semiempirical substituent effect models suitable for aromatic substituent effects in electrophilic reactions.

The SUMCHIN Substituent Effect Models. The Dewar substituent effect models are based on the concept of the interaction of substituent dipoles, and small charges induced by substituents, with the charge localized at the reaction center.[7] The obvious electronic difference between side-chain reactions of the sort correlated by the Dewar equations and electrophilic aromatic substitution, or electrophilic side-chain reactions,[8] is the stabilization of charge developed in the latter types of reaction by delocalization of charge within the aromatic system. Consequently, in the models we propose here for electrophilic reactions, the interactions of substituents with the delocalized charge are considered to be the dominant mechanisms of substituent effects. We refer to these models as SUMCHIN substituent effect equations because substituent constants are calculated from the *sum* of *ch*arge *in*teractions with substituents, based on a separation of substituent effects into resonance and field-inductive terms.

The energetically significant resonance effect for electrophilic reactions is considered to be the electromeric effect[9] because of the possibility of direct stabilization of transition state charge by substituents through resonance interaction with the charge delocalized to the substituent position. The measure of the importance of electromeric effects at a particular position should be related to the extent to which conjugation with the reaction center is possible. The simplest measure of the extent of conjugation possible at a particular position is the amount of charge delocalized to that position in the transition state; in other words, the electromeric resonance capabilities of substituents can be effective only insofar as charge is available to them for resonance stabilization. Therefore, we define the transmission coefficient for electromeric resonance effects to be Δq_{ij}, the difference in charge at the position *i* bearing the substituents between the ground state and the transition state for reaction at ring position *j*. In this study, Δq_{ij} values are obtained from CNDO/2 calculations[10] performed for the parent aromatic systems or the parent arylmethanes, $ArCH_3$, as models for the ground-state molecules, and the cations ArH^+ or $ArCH_2^+$ as models for the transition states. The change in charge (Δq_{ij}) at the substituent position is taken to be the sum of the charges on the carbon atom and the hydrogen atom bonded to it (the regional charge[11]), since the charge at the substituent position is partially delocalized onto the hydrogen atom substituent in the calculations. This sort of dependency of the electromeric effect on some index of the extent of conjugation with the reaction center has been proposed in other, earlier studies.[6,12]

The nonresonance interactions of a substituent with the delocalized transition-state charge could be of two types: the field effect due to direct electrostatic interactions through space, and the inductive effect which operates through polarization of bonds. It has been shown in many studies that substituent effects previously considered to be the result of inductive interactions can better be accounted for as electrostatic interactions between the field set up by a substituent dipole and the charge created at the reaction center.[13] Accordingly, we will treat the field-inductive effect simply as a field effect, while recognizing that a portion of the observed interaction may be due to an inductive factor. Describing the variation of the field effect should be adequate for describing the total field-inductive effect because the effects from field and inductive interactions can be expected to operate in the same direction in most cases.

We suggest that the dependence of the field effect on charge distribution can be accounted for by summing the field interactions of the substituent dipole with the charge at every position in the molecule. Dewar has used a summation term to account for the mesomeric-field effect[7] and Eaborn considered a similar suggestion for nonconjugated interactions,[12b] but a summation approach for the field effect has not previously been developed into a substituent effect model for electrophilic reactions. In accomplishing the summation, we have used two mathematical models for the electrostatic field effect, resulting in two equations for calculating substituent constants, the two SUMCHIN models.

(a) SUMCHIN1 Model. The potential energy of interaction, *V*, of a point charge placed in a field set up by a dipole, where the distance, *r*, between the charge and the dipole is large compared with the distance separating the ends of the dipole, shows an inverse squared dependence on distance.[14] There is also a

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[5] M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, **84**, 3548 (1962).

[6] M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, **84**, 3539 (1962).

[7] M. J. S. Dewar, R. Golden, and J. M. Harris, *J. Amer. Chem. Soc.*, **93**, 4187 (1971).

[8] L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, **81**, 3323 (1959).

[9] The electromeric effect is defined as a resonance effect arising from mutual conjugation between the substituent and reaction center through an intervening conjugated system.[6]

[10] (a) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, 5136 (1965). (b) Program 142 from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.; modified for use on a CDC 6400 computer by Dr. P. Mowery. (c) Experimental geometries were used where available, or those determined by reasonable analogy.

[11] Regional charge is the sum of the charges on a carbon atom and on any hydrogen atoms bonded to it: A Streitwieser, Jr., and R. G. Jesaitis in "Sigma Molecular Orbital Theory," O. Sinanoglu and K. B. Wiberg, Ed., Yale University Press, New Haven, Conn., 1970, p 197.

[12] (a) M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3350 (1952); (b) C. Eaborn and A. Fischer, *J. Chem. Soc. B*, 152 (1969); (c) D. S. Noyce and R. W. Nichols, *Tetrahedron Lett.*, 3889 (1972).

[13] *Cf.* L. M. Stock, *J. Chem. Educ.*, **49**, 400 (1972).

[14] (a) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); (b) F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938); (c) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 282–285.

Table I. Correlative Comparison of Substituent Models

Aromatic system	Corr coeff				n[a]	Data ref
	σ_p^+, σ_m^+ Model	Modified D-G model	SUMCHIN1	SUMCHIN2		
(a) Detritiation in Trifluoroacetic Acid						
2,3,4-X-1-T-Benzene[b]	0.975	0.960	0.976	0.977	9	*c, d, e, f*
2,4-X-1-T-Benzene	0.740	0.901	0.957	0.947	9	*g*
5-X-2-T-Thiophene	0.990	0.990	0.985	0.989	7	*h*
4,5-X-2-D-Thiophene	0.969	0.972	0.976	0.973	6	*i*
2,3,4,5,6,7,8-X-1-T-Naphthalene	0.866	0.892	0.976	0.975	30	12b
1,3,4,5,6,7,8-X-2-T-Naphthalene	0.887	0.878	0.983	0.987	29	12b
10-X-9-T-Phenanthrene	1.000	0.588	0.998	1.000	6	*j*
(b) Solvolysis of 1-Arylethyl Derivatives in 80% Ethanol–Water						
3,4-X-1-Phenyl	0.999	0.999	0.999	0.999	10	*k*
4,5-X-2-Furyl	0.991	0.991	0.994	0.996	7	17c
4,5-X-2-Thienyl	0.996	0.994	0.993	0.995	8	*m*
6-X-2-Naphthyl	0.985	0.996	0.999	0.995	5	*l*
5,6-X-2-Benzofuryl	0.983	0.995	0.998	0.998	9	*n*
5,6-X-2-Benzo[*b*]thienyl	0.997	0.992	0.997	0.996	8	This paper
4,5,6,7-X-2-Benzo[*b*]thienyl	0.919	0.975	0.971	0.983	14	This paper

[a] Number of data points in correlation. [b] Correlation does not include benzene itself, for which only an approximate rate was determined: R. Baker and C. Eaborn, *J. Chem. Soc.*, 5077 (1961). [c] R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 4927 (1961). [d] R. Baker, R. W. Bott, and C. Eaborn, *J. Chem. Soc.*, 2136 (1963). [e] K. C. C. Bancroft, R. W. Bott, and C. Eaborn, *J. Chem. Soc.*, 4806 (1964). [f] R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 97 (1972). [g] Detritiation in 96.77% CF_3CO_2H–0.82% H_2O–2.41% $HClO_4$: C. Eaborn and R. Taylor, *J. Chem. Soc.*, 2388 (1961). [h] Detritiation in trifluoroacetic acid–acetic acid mixtures: A. R. Butler and C. Eaborn, *J. Chem. Soc. B*, 370 (1968). [i] Dedeuteration in trifluoroacetic acid–acetic acid mixture: A. I. Shatenshtein, A. G. Kamrad, I. O. Shapiro, Yu. I. Ranneva, and E. N. Zvyagintseva, *Dokl. Akad. Nauk SSSR*, **168**, 364 (1966). [j] C. Eaborn, A. Fischer, and D. R. Killpack, *J. Chem. Soc. B*, 2142 (1971). [k] Unpublished data, D. S. Noyce and B. Bartman. [l] Solvolysis of 2-naphthyldimethylcarbinyl chlorides in 95% acetone–water: V. Baliah and P. Ananthakrishna Nadar, *Indian J. Chem.*, 9, 1399 (1971). [m] D. S. Noyce, C. A. Lipinski, and R. W. Nichols, *J. Org. Chem.*, **37**, 2615 (1972). [n] D. S. Noyce and R. W. Nichols, *ibid.*, **37**, 4306 (1972).

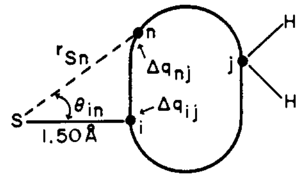

Figure 1. Diagram for SUMCHIN models.

dependence on the angle, θ, between the dipole axis and the line joining the charge to the dipole, and the magnitude of the effect is proportional to the magnitude of the charge, q, and the dipole moment, μ. This potential energy equation[14] (eq 2) usually incorporates a term describing the dependence on the effective dielectric constant, but to attempt to determine this factor which would vary slightly for each molecule[15] and probably within each molecule is not feasible or necessary for a simple substituent effect model. For interactions of a dipole with n number of charges, the potential energy will be given by eq 3.

$$V = (q\mu \cos \theta)/r^2 \tag{2}$$

$$V = \mu\sum\left(\frac{q \cos \theta}{r^2}\right)_n \tag{3}$$

Using the summation term in eq 3 as the transmission coefficient for the field effect and Δq_{ij} as the resonance transmission coefficient, we can combine the terms for the field and resonance effects into an equation for calculating substituent constants for electrophilic reactions (eq 4, the SUMCHIN1 model).

$$\sigma_{ij}^+ = D\sum\frac{\Delta q_{nj} \cos \theta_{in}}{r_{Sn}^{\,2}} + \Delta q_{ij}E^+ \tag{4}$$

The D and E^+ substituent parameters are calculated from Brown and Okamoto's σ_p^+ and σ_m^+ constants by using the appropriate transmission coefficients for benzene in eq 4 and then solving simultaneously the σ_p^+ and σ_m^+ equations for each substituent. D is a measure of the dipole field set up by the substituent, and E^+ describes the capability of a substituent for electromeric resonance interactions (with a positively charged system).

The Δq_{nj} are the changes in charge calculated for each atom, n, in the transition state resulting from reaction at ring position j. The field summation includes Δq_{ij}, which is the change in regional charge at the position to which the substituent is attached; all other charges are for individual atoms, calculated as previously described using CNDO/2.

Figure 1 illustrates the geometric relationships in the substituent model for ArH^+. For the purpose of calculating the field transmission coefficient, the center of the substituent dipole for all substituents is taken as 1.50 Å (an "average" bond distance) from the ring system along the substituent–ring bond axis, with the dipole moment directed along the bond. Thus, r_{Sn} is the distance in ångströms from the dipole center of the substituent S at position i to an atom n, and θ_{in} is the angle between the bond axis and a line drawn from n to the dipole center. The substituent dipole is considered to be the result of the distribution of electrons about the substituent atom or group of atoms, rather than the commonly used concept of a polarized substituent–ring bond with one end of the dipole at the ring carbon. The SUMCHIN1 model (eq 4) includes

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(15) C. Tanford, *J. Amer. Chem. Soc.*, **79**, 5348 (1957).

Table II. Field and Resonance Transmission Coefficients[a]

Parent compd	i	j	Δq_{ij}	$1/r_{ij}$	$\Sigma[(\Delta q_{nj} \cos\theta_{in})/r_{Sn}^2]$	$\Sigma(\Delta q_{nj}/r_{Sn})$
Benzene[b]	2	1	0.2070	1.00	0.143	0.367
	3	1	0.0334	0.577	0.0919	0.309
	4	1	0.2371	0.500	0.141	0.338
Thiophene[b]	4	2	0.0397	0.597	0.101	0.322
	5	2	0.2206	0.565	0.148	0.354
Naphthalene[b]	2	1	0.2405	1.02	0.147	0.356
	3	1	0.0060	0.575	0.0792	0.288
	4	1	0.2281	0.496	0.128	0.324
	5	1	0.0821	0.371	0.0698	0.271
	6	1	0.0457	0.329	0.0630	0.233
	7	1	0.1119	0.373	0.0794	0.248
	8	1	0.0127	0.559	0.0528	0.281
	1	2	0.2452	1.02	0.148	0.370
	3	2	0.1045	0.978	0.0964	0.303
	4	2	0.0427	0.575	0.0718	0.273
	5	2	0.0211	0.329	0.0588	0.255
	6	2	0.1331	0.276	0.0878	0.252
	7	2	0.0430	0.288	0.0650	0.240
	8	2	0.0894	0.373	0.0728	0.288
Phenanthrene[b]	10	9	0.2512	1.01	0.143	0.356
Benzene[c]	3	1	0.0353	0.577	0.0834	0.289
	4	1	0.2109	0.500	0.127	0.313
Furan[c]	4	2	0.0642	0.623	0.111	0.327
	5	2	0.2763	0.636	0.163	0.361
Thiophene[c]	4	2	0.0395	0.597	0.0923	0.302
	5	2	0.2051	0.565	0.136	0.331
Naphthalene[c]	6	2	0.1232	0.276	0.0814	0.239
Benzofuran[c]	5	2	0.0473	0.304	0.0701	0.247
	6	2	0.1377	0.306	0.0918	0.259
Benzo[*b*]thiophene[c]	4	2	0.1072	0.377	0.0776	0.278
	5	2	0.0398	0.297	0.0633	0.234
	6	2	0.1246	0.294	0.0840	0.246
	7	2	0.0322	0.362	0.0589	0.248

[a] See text for definitions. [b] ArH^+. [c] $ArCH_2^+$.

Table III. Field and Resonance Substituent Parameters

	Modified Dewar-Grisdale model		SUMCHIN1		SUMCHIN2	
Substituent	F^+	M^+	D	E^+	D	E^+
OCH_3	0.359	−4.54	2.85	−5.40	0.750	−4.80
SCH_3	0.525	−4.11	4.16	−5.36	1.10	−4.49
F	0.738	−2.10	5.85	−3.86	1.54	−2.63
Cl	0.770	−1.28	6.10	−3.12	1.61	−1.84
C_6H_5	0.282	−1.52	2.23	−2.19	0.588	−1.72
Br	0.769	−1.11	6.10	−2.96	1.61	−1.67
I	0.681	−0.976	5.40	−2.61	1.42	−1.47
CH_3	−0.028	−1.41	−0.223	−1.34	−0.059	−1.38
C_2H_5	−0.030	−1.33	−0.234	−1.26	−0.062	−1.31
$CH(CH_3)_2$	−0.026	−1.26	−0.210	−1.20	−0.055	−1.24
$C(CH_3)_3$	−0.033	−1.14	−0.258	−1.06	−0.068	−1.11
H	0.00	0.00	0.00	0.00	0.00	0.00
CO_2^-	−0.049	0.007	−0.387	0.121	−0.102	0.041
$Si(CH_3)_3$	0.015	0.064	0.121	0.025	0.032	0.052
$N(CH_3)_4^+$	0.589	0.539	4.67	−0.890	1.23	0.110
CF_3	0.846	0.897	6.71	−1.12	1.77	0.284
CN	0.915	0.956	7.26	−1.23	1.91	0.295
NO_2	1.10	1.14	8.70	−1.48	2.29	0.347
CO_2H	0.509	0.788	4.04	−0.432	1.06	0.417
$CO_2CH_2CH_3$	0.578	0.915	4.58	−0.464	1.21	0.498
CO_2CH_3	0.580	0.944	4.60	−0.439	1.21	0.527

the calculation of the electrostatic interaction of the substituent with the charge delocalized to the position to which it is attached, as part of the field effect.

The transmission coefficients used in SUMCHIN1 are listed in Table II for a variety of aromatic systems; substituent parameters, the D and E^+ values, are listed in Table III. The success of the model in rate correlations is summarized in Table I.

(b) SUMCHIN2 Model. We also propose another substituent effect model, eq 5, that differs from eq 4

$$\sigma_{ij}^+ = D\sum\frac{\Delta q_{nj}}{r_{Sn}} + \Delta q_{ij}E^+ \qquad (5)$$

in the form of the transmission coefficient for field effects. The summation using the simple $1/r$ attenuation factor for field effects is considered for two reasons. (i) As noted by Dewar and Grisdale,[6] when the distance between a dipole and a point charge is comparable to the length of the dipole, the potential energy of interaction varies less rapidly than predicted by a $1/r^2$ term. The use of a $1/r$ term is an approximation to correct for the close proximity of the substituent to the charge centers in the summation of field effects. (ii) In comparing a series of compounds differing only in the substituent occupying a particular position, the electrostatic effect on reactivity could be considered as arising from changing the charge density pattern in the region occupied by the substituents. It may be that the process of changing substituents resembles more the changing of a point charge in the region occupied by the substituent rather than a change in dipole, as far as the propagation of field effects is concerned. The potential energy of interaction of two point charges exhibits a $1/r$ dependence on distance, and therefore the field interaction of a point charge representing the substituent with delocalized charges can be treated as a summation of $1/r$ terms (eq 5, SUMCHIN2 model). Furthermore, the considerable discussion in the literature regarding the exact dependence of the field effect on distance[16] makes it desirable to evaluate the use of both $1/r$ and $\cos\theta/r^2$ as field-transmission coefficients in semiempirical models.

All of the symbols used in eq 5 (SUMCHIN2 model) have the same definitions as in eq 4 (SUMCHIN1). The values of the substituent parameters D and E^+ differ from the SUMCHIN1 model, but they are established in the same way from σ_p^+ and σ_m^+ constants. The application of SUMCHIN2, the substituent parameters, and the transmission coefficients used are summarized in Tables I–III.

Previous Semiempirical Approaches. For comparison with the SUMCHIN models, two methods used previously for the correlation of substituent effects in electrophilic aromatic reactions are briefly described here, and the results from their application are also summarized in Tables I–III.

A simple, convenient, and often successful[17] approach has been to apply σ_p^+ and σ_m^+ constants directly for the correlation of substituent effects in other systems. In this method, σ_p^+ constants are assigned to substituents at all positions which can formally be considered as conjugated[18] with the reaction center, and σ_m^+ constants are used for all nonconjugated positions. The method will be referred to as the σ_p^+, σ_m^+ model. This procedure obviously goes beyond the originally intended usage of σ_p^+ and σ_m^+, but evaluation of the σ_p^+, σ_m^+ model provides a useful basis for comparing other models.

The original Dewar–Grisdale equation[5] for substituent effects has been modified for application to electrophilic substitution by Bancroft and Howe[19] and also by Eaborn and Fischer.[12b] A similar modification was made in treating the solvolysis rates of heteroaryl carbinyl derivatives,[12c,20] and this latter modification is used here for comparison. The modified equation (eq 6) retains the same form as the original Dewar–Grisdale equation, but the field and resonance parameters (F^+ and M^+) are derived from benzene σ^+ constants instead of σ constants, and the resonance transmission coefficient, Δq_{ij}, differs from the original in being defined exactly as described in the SUMCHIN models. This modified Dewar–Grisdale model uses a simple $1/r_{ij}$ transmission coefficient for the field effect, where r_{ij} is the distance (in units of benzene C–C bond lengths) between the site i of substituent attachment and the ring position j at which the reaction occurs (or j may be the position to which the reactive side chain is attached).

$$\sigma_{ij}^+ = (F^+/r_{ij}) + \Delta q_{ij}M^+ \tag{6}$$

Results and Discussion

Correlative Evaluation. Table I presents the results of Hammett-type[21] correlations of rate data for protodetritiation and solvolysis of 1-arylethyl derivatives using the substituent constants calculated from the various models. It is clear from the table that the new SUMCHIN substituent models (eq 4 and 5) give consistently good representations of the observed effects. The modified Dewar–Grisdale model (eq 6) gives good results for the solvolysis studies, but gives poor results in most of the detritiation correlations. The σ_p^+, σ_m^+ model is satisfactory in some cases for correlating both detritiation and solvolysis, but it also gives poor results in several instances.

The best results for the σ_p^+, σ_m^+ model and the modified Dewar–Grisdale model are obtained when substituent effects are measured in systems where the orientation of substituents and the geometry of the ring systems closely resemble the meta- and para-substituted benzenes from which the models were parameterized. Thus, the mono ring systems, thiophene and furan, give excellent correlations in both models for substituents on the side of the ring opposite the reaction center (Table I). Good correlations are also seen for the 5 and 6 positions of benzo[*b*]thiophene and benzofuran, and the 6 and 7 positions of naphthalene in both models; these substituent positions are at the opposite end of the ring systems and have no unusual angles of orientation relative to the reaction center. The σ_p^+, σ_m^+ model often gives an apparently good description of the balance of field and resonance effects at individual positions (*cf.* 10-X-9-T-phenanthrene series), but fails completely for studies involving several positions in the same ring system because each position tends to give a correlation line with a slope differing from the slope at other positions.

The modified Dewar–Grisdale model gives some improvement over the σ_p^+, σ_m^+ model in the description of substituent effects at the 5 and 6 positions of benzo[*b*]thiophene and benzofuran; the improvement is

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(16) (a) P. R. Wells and W. Adcock, *Aust. J. Chem.*, **18**, 1365 (1965); (b) W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 379 (1967); (c) J. D. S. Ritter and I. Miller, *ibid.*, **86**, 1507 (1964); (d) H. D. Holtz and L. M. Stock, *ibid.*, **86**, 5188 (1964); (e) A. Buckley, N. B. Chapman, and J. Shorter, *J. Chem. Soc. B*, 195 (1969); (f) K. C. C. Bancroft and G. R. Howe, *ibid.*, 1221 (1971).

(17) (a) G. Marino, *Advan. Heterocycl. Chem.*, **13**, 236 (1971), and references therein; (b) D. A. Forsyth and D. S. Noyce, *Tetrahedron Lett.*, 3893 (1972); (c) D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, **34**, 1008 (1969).

(18) Positions to which charge is delocalized in simple valence-bond drawings of resonance structures of the carbonium ion intermediate.

(19) K. C. C. Bancroft and G. R. Howe, *Tetrahedron Lett.*, 4207 (1967).

(20) D. S. Noyce, C. A. Lipinski, and R. W. Nichols, *J. Org. Chem.*, 37, 2615 (1972).

(21) Least-squares fitting of log k_{rel} *vs.* calculated σ^+ constants.

due to a better description of the importance of resonance contributions of substituents at the 5 position by eq 6 than by σ_m^+.[22] However, the modified Dewar–Grisdale model fails to account for the effects of substituents in a position adjacent to the reaction center (ortho-type position), as exemplified by the lack of correlation for the "ortho" substituted phenanthrene series. The use of the simple $1/r_{ij}$ factor in eq 6 for the field-transmission coefficient greatly overemphasizes the importance of the field effect in ortho situations because of the small magnitude of r_{ij}: compare the $1/r_{ij}$ coefficients for ortho situations with the others in Table II. Use of the $1/r_{ij}$ factor is the reason ortho and peri substituents in naphthalene show serious deviations from the correlation line in the modified Dewar–Grisdale model, as was previously observed by Eaborn for his model of the same type.[12b] The Eaborn model actually yielded somewhat better correlation coefficients for naphthalene than those reported here for the modified Dewar–Grisdale model, because the Eaborn model used HMO calculations which overestimate the magnitude of Δq_{ij}, the resonance transmission coefficient, in the ortho positions, thereby producing a better approximation of the balance of field and resonance effects by compensating somewhat for the overemphasis of field effects in the ortho positions.

Significant improvements in correlation coefficients are realized through the use of SUMCHIN models for substituent effects in the protodetritiation studies. The most dramatic example in Table I is the excellent correlation obtained for the "ortho" substituted phenanthrene series. The improvement in the other cases is also due chiefly to great improvement in the description of ortho substituent effects. There are only two significant differences in correlation coefficients between the SUMCHIN1 and SUMCHIN2 models; SUMCHIN2 gives slightly better results for the 4,5,6,7-X-2-benzo[*b*]thienyl series and slightly poorer results for the 2,4-X-1-T-benzene series.

Predictive Evaluation. If calculated substituent constants are to be of use for accurate predictions of reactivities, the response of the system to substituent effects, as represented by the Hammett ρ, must be known. The magnitude of ρ is a measure of the magnitude of the charge developed in the reaction and of the extent to which substituents are able to interact with the charge.[17b,23] However, the SUMCHIN substituent models proposed in this paper are based on descriptions of substituent interactions with charge distributions, so that the calculated substituent constants reflect not only the balance of field and resonance effects but also the extent to which substituents are able to interact with the charged system. Therefore, if the magnitudes of the substituent constants are properly scaled in the models, the magnitude of ρ will be a measure only of the magnitude of the charge developed in the system during the reaction. The ρ value is thus considered to be a constant characteristic of a reaction, regardless of the substrate, as long as similar transition states with similar charge development hold for all the aromatic substrates considered. The assumption of the same transition state for all substrates is implicit in the semiempirical models proposed here, because in the MO calculations of charge distribution, each model molecule gains a full unit of positive charge in the transition state, thereby creating a calculational representation in which the reaction for each aromatic substrate is considered to have progressed to the same extent along the reaction coordinates.

Table IV summarizes the results of comparing calculated σ^+ constants with observed σ^+ constants. The σ^+_{obsd} were obtained from the experimental log k_{rel} data by assuming the general applicability of the ρ value observed for meta- and para-substituted benzenes to all aromatic systems under the same reaction conditions.[24] The table lists the slopes, intercepts, correlation coefficients, and standard deviations from the least-squares fittings of σ^+_{obsd} against σ^+_{calcd} using all of the nonbenzenoid substituent effect data from the studies listed in Table I. Figures 2a–d illustrate the differences between the models in prediction of σ^+ values for protodetritiation.

Table IV. Least-Squares Fitting of σ^+_{obsd} *vs.* σ^+_{calcd}: $\sigma^+_{\text{obsd}} = m\sigma^+_{\text{calcd}} + i$

Model	*m*	*i*	Corr coeff	SD
	(a) Detritiation			
σ_p^+, σ_m^+ model	0.798	0.023	0.882	0.14
Modified Dewar–Grisdale model	0.855	−0.066	0.897	0.15
SUMCHIN1 model	1.091	0.0085	0.969	0.084
SUMCHIN2 model	1.021	−0.017	0.972	0.080
	(b) Solvolysis			
σ_p^+, σ_m^+ model	0.815	0.044	0.923	0.15
Modified Dewar–Grisdale model	1.059	0.026	0.985	0.066
SUMCHIN1 model	1.016	−0.0014	0.985	0.066
SUMCHIN2 model	1.045	−0.0088	0.987	0.062

The agreement between the calculated and observed σ^+ constants is very good for the SUMCHIN models. The quality of the correlations is equivalent to that obtained by Dewar in his improved treatment (FMMF model) of substituent effects on the pK_A of carboxylic acids.[7] SUMCHIN2 appears to be slightly better than SUMCHIN1, although the difference is probably not significant. The slopes in both cases are close to unity, and the intercepts are near zero. Clearly, the use of substituent constants calculated from either SUMCHIN model in conjunction with the ρ established for benzene yields good predictions of relative reactivities. Apparently the benzene ρ value is appropriate for all the systems, thus indicating a similar degree of charge development in all the substrate series. The one significant exception to the constancy of ρ is the thiophene correlations, for which the slope of σ^+_{obsd} *vs.* σ^+_{calcd} in all models is 20–25% greater than unity for both hydrogen isotope exchange and solvolysis reactions; this deviation is thought to be caused by an inadequacy in the CNDO/2 method for the calculation of charge distributions in sulfur-containing

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(22) D. S. Noyce and R. W. Nichols, *J. Org. Chem.*, 37, 4306 (1972).

(23) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 177.

(24) The benzene ρ values were those observed at the same temperatures used for the other studies, using calculated σ^+ constants for benzene; benzene σ^+_{calcd} values are equivalent to σ_p^+ and σ_m^+ for solvolysis, but differ slightly for each model for detritiation.

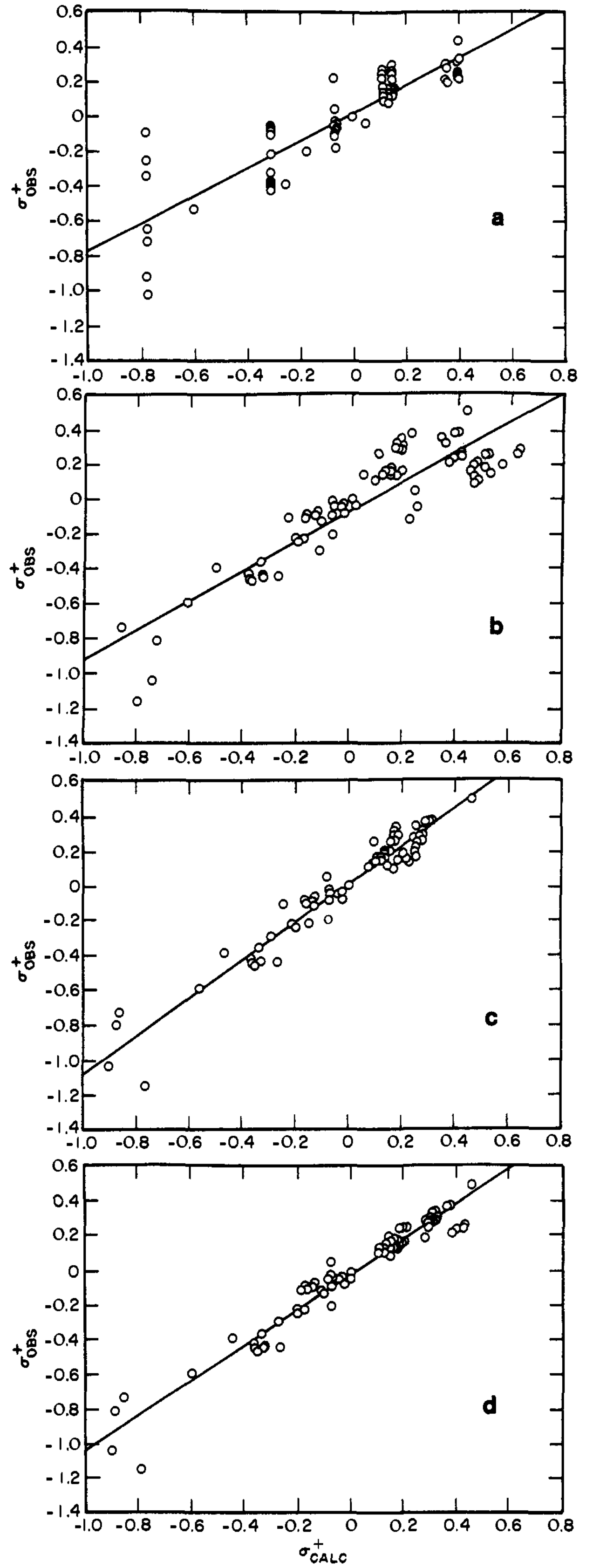

Figure 2. Plots of least-squares fitting of σ^+_{obsd} *vs.* σ^+_{calcd} for protodetritiation data in aromatic systems other than benzene: (a) σ_p^+, σ_m^+ model; (b) modified Dewar-Grisdale model; (c) SUMCHIN1 model; (d) SUMCHIN2 model.

compounds, as we have briefly discussed in a previous paper.[17b]

The σ_p^+, σ_m^+ model and the modified Dewar-Grisdale model are not as successful as the SUMCHIN models in predicting σ^+ values. The failure of the modified Dewar-Grisdale model is due primarily to its poor description of certain substituent situations, such as ortho-substituted systems; in the solvolysis studies where good correlations obtain, the magnitudes of substituent constants are scaled well so that the σ^+_{calcd} closely match the σ^+_{obsd}. However, the failure of the σ_p^+, σ_m^+ model in prediction is due not only to poor correlations but also to variations in the ρ values for the correlation lines, due to the lack of any flexibility in the magnitude of the σ^+_{calcd} which are simply the σ_p^+ and σ_m^+ constants.

Substituent Parameters. The field and resonance substituent parameters for the modified Dewar-Grisdale model and the SUMCHIN models are listed in Table III. Since these models are based on the separation of substituent effects into independent field and resonance components, ideally the values of the parameters should represent the potential of each substituent for affecting the stability of the positively charged activated complex relative to the ground state, through the mechanisms of field and resonance interactions. It is somewhat difficult to evaluate the degree to which the parameters properly represent these potentials; indeed, if accurate theoretical values were available for comparison, it would be unnecessary to use these semiempirical models. However, it is possible to compare the parameters with results of other studies, and in terms of qualitative theoretical expectations.

The sets of D and E^+ substituent parameters in Table III were established by solving simultaneously the substituent effect equations for para- and meta-substituted benzenes (eq 7 and 8), using the appropriate field and resonance transmission coefficients for each SUMCHIN model.

$$\sigma_p^+ = (\text{para field})D + (\Delta q_p)E^+ \qquad (7)$$

$$\sigma_m^+ = (\text{meta field})D + (\Delta q_m)E^+ \qquad (8)$$

The F^+ and M^+ parameters were defined in the same way for the modified Dewar-Grisdale model (eq 6). For all three models, the field and resonance transmission coefficients used (Table II) were determined from the changes in charge calculated for the process $C_6H_5CH_3 \rightarrow C_6H_5CH_2^+$, and the σ^+ constants were those of Brown and Okamoto.[2]

The sets of field parameters (F^+ and D values) are essentially the same for each model, with each set differing from the others only by a constant proportionality factor. This proportionality between sets can be seen to be the derivational result of using the same transmission coefficients for resonance (Δq_p and Δq_m) for all three models in eq 9, the solution of

$$D = \frac{(\Delta q_m)\sigma_p^+ - (\Delta q_p)\sigma_m^+}{(\Delta q_m)(\text{para field}) - (\Delta q_p)(\text{meta field})} \qquad (9)$$

eq 7 and 8 for D. Qualitatively, the field parameters reflect the usual conceptions of field or inductive effects,[25] with the alkyl and negatively charged carboxylate groups being the only substituents stabilizing a positive charge. The relative magnitudes of the parameters

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[25] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 207.

are also reasonable; one way of illustrating this is by analyzing the parameters in the Swain and Lupton treatment,[26] which indicates a 91% $\mathcal{F}$ component in the set.[27]

The substituent parameters representing the potential of substituents for electromeric resonance interaction were obtained from the general eq 10, the solution of eq 7 and 8 for E^+.

$$E^+ = \frac{(\text{meta field})\sigma_p^+ - (\text{para field})\sigma_m^+}{(\text{meta field})(\Delta q_p) - (\text{para field})(\Delta q_m)} \qquad (10)$$

Electromeric resonance potentials should be represented by parameters which reflect only the capability of substituents for stabilization of a positive charge by electron release and charge delocalization. CNDO/2 calculations on substituted benzenes for the transformation $ArCH_3$ to $ArCH_2^+$ show that the change in regional charge at the side chain is nearly constant except in the benzenes substituted with an electron-donating group in the para position.[3] The calculations suggest that electromeric interaction is significant for electron-releasing substituents, but small for substituents which are potentially electron withdrawing; the reverse situation should hold for electromeric interaction with a negatively charged system.[7,28] Experimental support for the calculations comes from studies of multiple substituted systems:[29] electron-releasing substituents tend to "saturate" carbonium ions toward further stabilization by other substituents, while the effects of destabilizing groups are more nearly additive.[29a] These results are consistent with the idea that electron-releasing substituents reduce the charge available to other substituents for stabilization, while the destabilizing groups have only a small effect on the distribution of transition state charge. Thus, if we assume electromeric stabilization correlates with release of electron density from substituents, the expectation is for electromeric resonance parameters to show a range of values from significantly stabilizing (negative values) to near zero.

The E^+ values (Table III) for the SUMCHIN2 model show the closest relation to the expectations described above for electromeric parameters. It should be noted from eq 10 that the relative values of the resonance parameters in any particular model depend upon the relative magnitudes of the field transmission coefficients for the meta and para positions of benzene; if there is an inductive effect of any significance which does not precisely parallel the field effect, the result will be a deviation of the resonance parameters from values which might be expected theoretically. Further, it should be noted that the parameters in the SUMCHIN models were obtained by assuming a standard substituent–ring bond length (1.50 Å). Slightly different sets of resonance parameters would be obtained if the distance from the ring to the assumed dipole center was allowed to vary with the type of substituent, an impractical but theoretically more valid approach. The SUMCHIN1 model is particularly sensitive to distance effects, because a $1/r^2$ term varies more rapidly with distance than a $1/r$ term as used in SUMCHIN2.

Benzo[*b*]thiophene. As part of this study of substituent effects in aromatic systems, we have sought to provide additional quantitative data for substituents in aromatic systems other than benzene. We report new data here for the rates of solvolysis of a series of substituted 1-(2-benzo[*b*]thienyl)ethyl *p*-nitrobenzoates in 80% ethanol–water (Table V).[30] This study was designed to test the limits of applicability of the substituent effect models to solvolytic reactivity. Earlier studies of solvolysis of substituted aromatic systems (see Table I) were insufficient to distinguish adequately between possible models, as all four methods gave reasonably good correlations.

Table V. Rates of Solvolysis of Substituted 1-(2-Benzo[*b*]thienyl)ethyl *p*-Nitrobenzoates in 80% Ethanol–Water at 75°

Substituent	k, sec^{-1}	log k_{rel}
H	1.28×10^{-5}	0.00
4-OCH_3	1.29×10^{-4}	1.00
4-CH_3	4.04×10^{-5}	0.500
4-Cl	4.84×10^{-7} [a]	−1.42
5-OCH_3	3.19×10^{-5}	0.398
5-CH_3	3.29×10^{-5}	0.411
5-Cl	7.77×10^{-7} [a]	−1.22
5-NO_2	2.28×10^{-8} [b]	−2.75
6-OCH_3	2.88×10^{-3}	2.35
6-CH_3	1.15×10^{-4}	0.954
6-Cl	2.97×10^{-6}	−0.633
7-OCH_3	1.12×10^{-5}	−0.059
7-CH_3	2.03×10^{-5}	0.202
7-Cl	3.60×10^{-7} [b,c]	−1.55

[a] Extrapolated from rates at higher temperatures. [b] Computed from the rate for the chloride, using log (k_{Cl}/k_{OPNB}) = 4.875. [c] Extrapolated from rates at lower temperatures.

The results observed for a series of 5-substituted and 6-substituted 1-(2-benzofuryl)ethanol derivatives in an earlier study indicated that σ_p^+ values gave an excellent description of substituent effects from the 6 position, but σ_m^+ did not give as good a correlation at the 5 position; the modified Dewar–Grisdale model (eq 6) gave a high quality correlation for both positions.[22] The results for the solvolysis of 5- and 6-substituted 1-(2-benzo[*b*]thienyl)ethyl *p*-nitrobenzoates exhibit a very similar pattern: the log k_{rel} for the 5- and 6-substituted benzo[*b*]thiophenes correlate excellently against the log k_{rel} for the benzofuran series (correlation coefficient = 0.999+).

It was hoped that the determination of substituent effects at the 4 and 7 positions of benzo[*b*]thiophene would make possible further distinctions between model equations, because substituents at these positions have a definite angle of inclination relative to the bulk of the 1-(2-benzo[*b*]thienyl)ethyl system (Figure 3). In fact, the σ_p^+, σ_m^+ model is clearly shown to be inadequate (Figure 4a) and the modified Dewar–Grisdale model does not give as good a correlation

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(26) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

(27) The set evaluated includes all substituents in Table III except the isopropyl and carbomethoxy groups, for which $\mathcal{F}$ and $\mathcal{R}$ values are not available.

(28) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, pp 414–419.

(29) (a) S. V. McKinley, J. W. Rakshys, Jr., A. E. Young, and H. H. Freedman, *J. Amer. Chem. Soc.*, **93**, 4715 (1971); (b) J. W. Rakshys, Jr., S. V. McKinley, and H. H. Freedman, *Chem. Commun.*, 1180 (1969); (c) S. Nishida, *J. Org. Chem.*, **32**, 2697 (1967); (d) L. D. McKeever and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 4544 (1966).

(30) Experimental details: D. S. Noyce and D. A. Forsyth, manuscript in preparation.

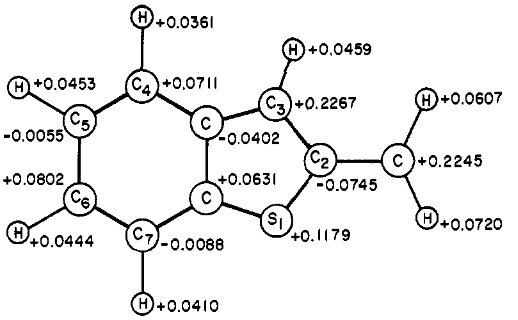

Figure 3. Changes in charge, $\Delta_{q_{02}}$, from 2-methylbenzo[*b*]thiophene to 2-benzo[*b*]thienyl cation, calculated using CNDO/2.

for the 4,5,6,7-substituted series as for the 5,6-substituted series (see Table I). However, in this case the SUMCHIN1 model shows no improvement over the modified Dewar–Grisdale model.

The plot of log k_{rel} *vs.* $\sigma^{+}_{\text{calcd}}$ from the SUMCHIN1 model (Figure 4b) indicates a clear regularity in the deviations: substituents at the 4 position do not lie on the correlation line established by the other substituents. The deviations are in the direction which suggests that either resonance effects are less important or field effects are more important than predicted. It is clearly a miscalculation of the balance of field and resonance effects rather than inaccurate scaling of the magnitude of the constants, because an adequate line cannot be drawn through the 4-OCH_3, 4-CH_3, H, and 4-Cl points when considered separately.

SUMCHIN2 (eq 5) gives better results than SUMCHIN1 (eq 4) for the benzo[*b*]thiophene data (Figure 4c), although the correlation is still not of the excellent quality seen if results from the 4 position are omitted. The improvement is due to a relative increase in the calculated importance of the field effect. Specifically, field interaction with the substantial charge at position 3 (Figure 3) is given more weight in the SUMCHIN2 model than in SUMCHIN1 where the cos θ factor considerably reduces the calculated interaction with charge at the 3 position. More studies in other systems should be conducted to determine whether there is a basic inadequacy in the model equations, or if the observed deviations from the predictions are specific to the benzo[*b*]thiophene system. In this regard it should be noted that the analogous position in naphthalene (the 8-X-2-T-naphthalene series) in detritiation shows no unusual deviations of substituent effects from those predicted by either SUMCHIN model. One possible source of inaccuracy other than a failure of the models themselves is in the molecular orbital calculations, which perhaps may not give accurate representations of the charge distribution in sulfur-containing compounds.

Conclusions

The use of semiempirical mathematical models to calculate the perturbational effects of substituents on aromatic reactivity is a successful and practical approach. We have demonstrated that models based on descriptions of field and electromeric resonance interactions with delocalized transition state charge (the SUMCHIN models) successfully predict the rates of reaction for a wide variety of substituted aromatic systems, in both electrophilic aromatic substitution and electrophilic side-chain reactions.

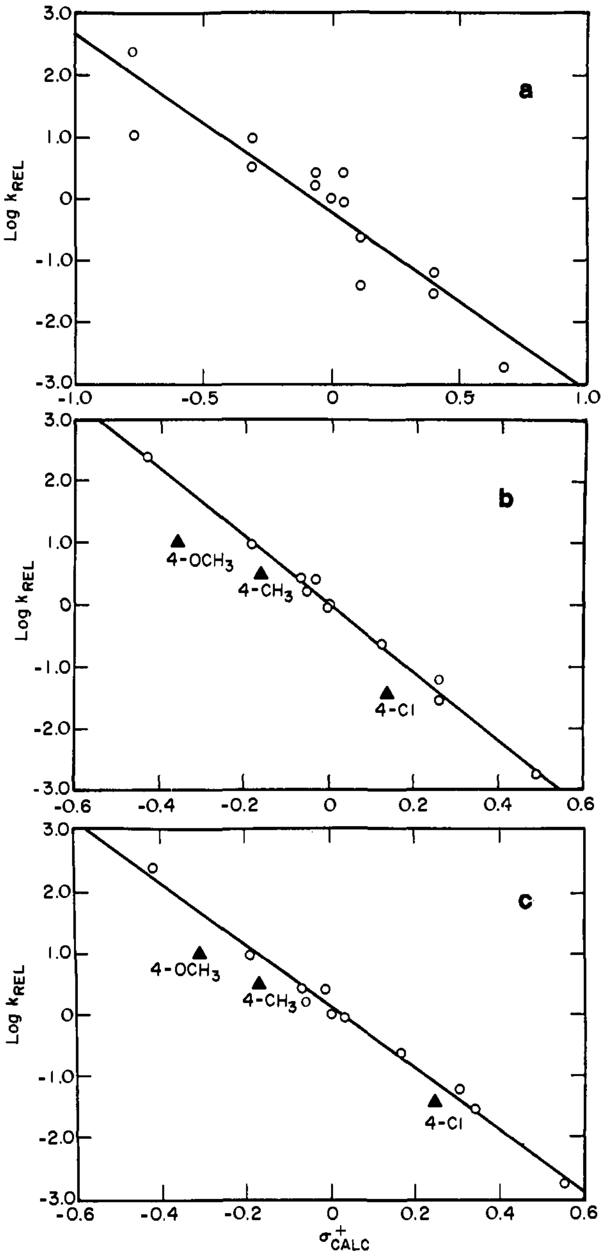

Figure 4. The log k_{rel} for solvolysis of 1-(2-benzo[*b*]thienyl)ethyl *p*-nitrobenzoates correlated *vs.* $\sigma^{+}_{\text{calcd}}$: (a) σ_p^{+}, σ_m^{+} model; (b) SUMCHIN1 model; (c) SUMCHIN2 model.

In a paper on reactivity relationships for substituent effects in aromatic systems, Bancroft and Howe suggest that the degree of precision obtained in fitting calculated effects to experimental data reflect the validity of the mathematical model chosen, and also the validity of the underlying theoretical assumptions.[16f] On this basis, the results discussed in this paper clearly indicate that the SUMCHIN models (eq 4 and 5) are more valid than any approaches previously used. Since the improved correlations arise from models which describe the field effect of substituents as a summation of interactions with charges developed in the transition state, the results imply that such a summation provides a valid description of substituent field effects on the reactivity of aromatic systems in electrophilic reactions. This concept of the source of field effects is a major difference between models and the available data serve to distinguish the generally successful SUMCHIN models from those which are fundamentally incapable of describing certain substituent situations. However, less fundamental differences between models, such as the precise form of the field transmission coefficient in the SUMCHIN models, cannot be adequately evaluated from the present evidence. Indeed, if a few key series of substituent data were missing, it would be difficult to distinguish between any of the possible approaches. This points to the need for carefully designed studies to test the limits of applicability of substituent models; such tests may provide information for the further elucidation of the mechanisms of substituent effects.

Carefully designed substituent effect studies will help establish the best form for a substituent model, but the very nature of a semiempirical approach that makes it both practical and reasonably accurate also makes such distinctions difficult and somewhat limits its theoretical value. A semiempirical model is parameterized from experimental data so that regardless of its functional form it will reproduce exactly the correct results if it is applied to the system from which it was parameterized; it should also produce good results when applied to other systems which closely resemble the basis system. As long as the functional forms of the model equations approximate the "true" dependence of substituent effects on factors which vary between positions in aromatic systems, the process of parameterizing the equations from experimental data allows this type of semiempirical approach to produce excellent practical results, while showing a certain insensitivity to the precise form of the mathematical model. Furthermore, any interaction not explicitly accounted for in the model will be accommodated to some extent in the derived substituent parameters. For these reasons, we are also investigating other means of evaluating the variation of substituent effects in aromatic systems.

Acknowledgments. I would like to express my gratitude to Professor Donald S. Noyce for his suggestions and support in my work with him, and to Professor Andrew Streitwieser, Jr., for helpful discussions. I wish also to acknowledge helpful comments from B. Sandel, B. Bartman, and R. W. Nichols.

Intermediates in Nucleophilic Aromatic Substitution. IX.[1] 1:1 and 1:2 Sulfite Complexes of 1,3,5-Trinitrobenzene. Cis–Trans Isomerism in the 1:2 Complex

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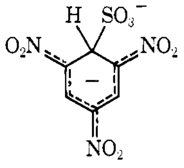
Abstract: A kinetic study by the stopped-flow method of the interaction of 1,3,5-trinitrobenzene with sulfite ion shows that three different anionic σ complexes are formed. The fastest process is associated with the reversible formation of a 1:1 complex, the two slower processes with the reversible formation of two different 1:2 complexes (TNB:SO_3^{2-} = 1:2). Evidence based on absorption spectra, reaction rates, and equilibrium properties indicates the two 1:2 complexes to be cis and trans isomers.

Sodium sulfite reacts with 1,3,5-trinitrobenzene (TNB) to yield the typically highly colored Jackson–Meisenheimer[3,4] complex. It has been shown that in aqueous solution both a 1:1 complex[5] (**1**) and a 1:2 complex[6] (**2**) are formed, depending upon the sulfite concentration. Previous investigators have determined equilibrium constants of complex formation from spectrophotometric data,[6,7] recorded nmr spectra[6] of both complexes (**1** and **2**), and isolated the 1:2 TNB–sulfite complex as a dark red crystalline material.[8]



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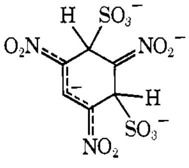

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Crampton[6] has reported nmr spectra of several other 1:2 complexes formed between sulfite ion and N-substituted picramides. Interestingly, it was observed that when the RR′N group of the complex was symmetrically substituted (R = R′), the sp^3 ring protons in the complex were equivalent, giving only a single peak. However, if the complex was unsymmetrically substituted (*i.e.*, Me–N–Ph), the sp^3 ring protons were nonequivalent and two resonance lines resulted. Strauss[9] has offered several possible interpretations for this result; one of them is that the nmr spectrum is actually that of an equimolar mixture of cis and trans

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(1) Part VIII: C. F. Bernasconi and R. H. de Rossi, *J. Org. Chem.*, **38**, 500 (1973).

(2) Alfred P. Sloan Fellow, 1971–1973.

(3) C. J. Jackson and F. H. Gazzolo, *J. Amer. Chem. Soc.*, **23**, 376 (1900).

(4) J. Meisenheimer, *Justus Liebigs Ann. Chem.*, **323**, 205 (1902).

(5) F. Čůta and E. Beránek, *Collect. Czech. Chem. Commun.*, **23**, 1501 (1958).

(6) M. R. Crampton, *J. Chem. Soc. B*, 1341 (1967).

(7) A. R. Norris, *Can. J. Chem.*, **45**, 175 (1967).

(8) R. A. Henry, *J. Org. Chem.*, **27**, 2637 (1962).

(9) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).