The Nature of the *ortho* Effect. I. Electrophilic Aromatic Substitution

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ortho, meta, and *para* partial rate factors for 19 sets of electrophilic aromatic substitution data were correlated with the extended Hammett equation $Q_X = \alpha\sigma_{I,X} + \beta,\sigma_{R,X} + h$. Significant correlations were obtained for 17 out of the 19 sets of *ortho* partial rate factors, 13 out of 15 sets of *meta,* and 17 out of 19 sets of *para.* We find that in the sets studied there is no significant steric effect. The results indicate that $\alpha_o = \alpha_p$ and $\beta_o = 0.77\beta_p$. The equality of α_o and α_p is accounted for in terms of the geometry of the transition state. The observation that the resonance effect for *ortho* substitution is smaller than that for *para* is in accord with the literature. The composition of the *ortho* electrical effect may be written $\epsilon_o = \beta_o/\alpha_p = 0.77\epsilon_p$. These results indicate that the *ortho–para* product ratio is given by $\log (p_o/2p_p) = \beta'\sigma_R + h'$. Thus the *ortho–para* product ratio is dependent solely upon the resonance effect of the substituent.

We have for some time been engaged in investigation of the effect of *ortho* substituents upon physical properties and chemical reactivity. In this paper we extend our studies to the effect of *ortho* substituents upon electrophilic aromatic substitution.[1] It has been suggested by de la Mare and Ridd[2] on the basis of a parallelism in the *para–meta* and *ortho–meta* product ratios that the *ortho* effect in nitration is primarily electronic in nature. They suggest, however, that halogenation of *ortho*-substituted benzenes is dependent at least in part on steric effects. We have two purposes in this work; the first is to determine the validity of the proposal of de la Mare and Ridd; the second is to investigate the magnitude and composition of the *ortho* electrical effect. To this end, we have examined the correlation of partial rate factors taken from the literature for 19 sets of aromatic substitution data with the extended Hammett equation. The reactions studied

$$Q_X = \sigma_{I,X} + \sigma_{R,X} + h \qquad (1)$$

include detritiation, nitration, chlorination, bromination, mercuration, and alkylation. The correlations were made by multiple linear regression analysis. The σ_I constants are taken from our collection;[3] the σ_R constants are from

$$\sigma_R = \sigma_p - \sigma_I \qquad (2)$$

The necessary σ_p values are from McDaniel and Brown[4] with the exception of that for the phenoxy group.[5] The data used in the correlations are presented in Table I.

Results

The results of the correlations are presented in Table II.

ortho **Partial Rate Factors.**—Sets 1, 6, 9, and 15 gave excellent correlation; the results obtained for set 8 were very good; set 13 gave good results; sets 10 and 14 gave fair results. For sets 3, 5, 7, 11, 12, 16, 18, and 19 poor but significant correlation was obtained. Exclusion of the value for X = I in set 3 gave good results. Exclusion of the value X = NHAc in set 5 gave excellent results. Sets 4 and 17 did not give significant correlation. The results for set 4 were improved by the exclusion of X = Ph (set 4A). The results for set 2 were not considered significant as α and β differed in sign.

meta **Partial Rate Factors.**—Excellent correlations were obtained for sets 1, 5, 6, 8, 12, 13, 14, and 15. Very good results were obtained for set 16, good results for sets 17 and 19. The results obtained for sets 3 and 7 were not significant. The results of sets 2 and 18 are considered to be not significant owing to the difference in sign between α and β. Exclusion of the value X = I gave fair results for set 2.

para **Partial Rate Factors.**—Excellent correlation was obtained for sets 1, 6, and 14; sets 8, 12, and 13 gave very good results. Exclusion of the value X = NHAc gave excellent results for set 8 (set 8A). Good results were obtained for sets 2, 15, and 16; exclusion of the value X = I from set 2 gave excellent results (set 2A). Sets 3, 5, 7, 9, 10, 11, 18, and 19 gave poor but significant correlation. Exclusion from set 5 of the values for X = NHAc and Ph resulted in an excellent correlation (set 5A). Sets 4 and 17 did not give a significant correlation; exclusion of the value X = Ph from set 4 gave some improvement but the correlation remained not significant (set 4A).

The results seem to show that partial rate factors are well correlated with eq 1. It is of particular interest to note that, of the *ortho*-substituted sets which gave poor but significant correlation, five had only four members. Of the *para*-substituted sets which gave poor but significant correlation, five out of seven had only four members. We believe that, had more data been available for these sets, the correlation would be much improved.

Discussion

The *ortho* Substituent Effect.—In addition to the loalized and delocalized electrical effects characteristic of any substituent bonded to sp^2-hybridized carbon atoms, *ortho* substituents are also capable in some cases of proximity effects of various types. We may represent the effect of *ortho* substituents by an equation analogous to that proposed by Taft[6] (eq 3), where ζ is

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + \psi\zeta_X + h \qquad (3)$$

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[1] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

[2] P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworth and Co. (Publishers) Ltd., London, 1959, pp 82, 142.

[3] M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).

[4] D. H. McDaniel and H. C. Brown, *ibid.*, **23**, 420 (1958).

[5] M. Charton, *J. Chem. Soc.*, 5884 (1964).

[6] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 565.

a parameter characteristic of the proximity effect of the X substituent and ψ is its coefficient. The proximity effect may consist of any combination of the following contributions: (1) intramolecular hydrogen bonding between substituent and reaction site; (2) intramolecular van der Waals and London forces between substituent and reaction site; (3) steric inhibition of resonance either between reaction site and skeletal group or substituent and skeletal group or both; (4) steric interference with solvation; (5) steric inhibition of the reagent. For our present purposes we shall make no attempt to dissect the proximity effect into contributions but simply consider the over-all proximity effect.

We may now consider a number of special cases of interest. (1) The proximity effect is zero. In this case eq 3 simplifies to

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \qquad (1)$$

(2) ζ_X = constant. Equation 3 now simplifies to

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h' \qquad (4)$$

where $h' = h + \psi\zeta_X$. Equation 4 is equivalent to eq 1. (3A)

$$\zeta_X = m\sigma_{I,X} + c \qquad (5)$$

Then

$$Q_X = (\alpha + m\psi)\sigma_{I,X} + \beta\sigma_{R,X} + h + \psi c \qquad (6)$$

$$Q_X = \alpha'\sigma_{I,X} + \beta\sigma_{R,X} + h' \qquad (7)$$

Equation 7 is equivalent to eq 1. (3B)

$$\zeta_X = m\sigma_{R,X} + c \qquad (8)$$

Then

$$Q_X = \alpha\sigma_{I,X} + (\beta + m\psi)\sigma_{R,X} + h + \psi c \qquad (9)$$

$$Q_X = \alpha\sigma_{I,X} + \beta'\sigma_{R,X} + h' \qquad (10)$$

Equation 10 is equivalent to eq 1. (3C)

$$\zeta_X = m\sigma_{I,X} + n\sigma_{R,X} + c \qquad (11)$$

Then

$$Q_X = (\alpha + m\psi)\sigma_{I,X} + (\beta + n\psi)\sigma_{R,X} + \psi c + h \qquad (12)$$

$$Q_X = \alpha'\sigma_I + \beta'\sigma_R + h' \qquad (13)$$

Equation 13 is again equivalent to eq 1. (4A) $\alpha\sigma_{I,X} \cong \beta\sigma_{R,X} \gg \psi\zeta_X$. Then

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \qquad (1)$$

(4B) $\psi\zeta_X \cong \alpha\sigma_{I,X} = \beta\sigma_{R,X}$. In this case eq 3 applies. (4C) $\zeta_X \gg \alpha\sigma_{I,X} \cong \beta\sigma_{Y,X}$. Then

$$Q_X = \psi\zeta_X + h \qquad (14)$$

(5A) $\sigma_{I,X} = 0$. Then

$$Q_X = \beta\sigma_{R,X} + \psi\zeta_X + h \qquad (15)$$

(5B) $\sigma_{R,X} = 0$. Then

$$Q_X = \alpha\sigma_{I,X} + \psi\zeta_X + h \qquad (16)$$

(5C) $\sigma_{I,X} = \sigma_{R,X} = 0$. Then

$$Q_X = \psi\zeta_X + h \qquad (17)$$

(6A) $\sigma_{I,X}$ = constant.

$$Q_X = \beta\sigma_{R,X} + \psi\zeta_X + h' \qquad (18)$$

where $h' = \alpha\sigma_{I,X} + h$. (6B) $\sigma_{Q,X}$ = constant.

$$Q_X = \alpha\sigma_I + \psi\zeta_X + h' \qquad (19)$$

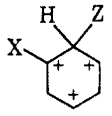
where $h' = \beta\sigma_{R,X} + h$. (6C) $\sigma_{I,X}$ = a constant, $\sigma_{R,X}$ = a constant. Then

$$Q_X = \psi\zeta_X + h' \qquad (20)$$

where $h' = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h$.

The results of the correlations have shown that the partial rate factors for *ortho* substitution are correlated successfully by eq 1. Then we may exclude cases 4B, 4C, 5A, 5B, 5C, 6A, 6B, and 6C. Thus the proximity effects must be either 0, constant, or a linear function of σ_I, σ_R, or both. Of the contributions to the proximity effect we have cited, only the van der Waals and possibly the London interactions between reaction site and substituent should lead to a relationship between ζ and σ_I or σ_R or both. We infer then that certainly all of the other contributions to the proximity effect are either constant or zero and that in accord with the suggestion of de la Mare and Ridd the effect of *ortho* substituents upon electrophilic aromatic substitution is primarily an electrical effect.

Localized *ortho* Electrical Effect.—To make possible a comparison of α_o with α_p we have carried out a correlation by means of simple regression analysis. The results of the correlation are given in Table III; they show that the α values are equal for *ortho* and *para* substitution. To account for this observation let us consider the intermediate in electrophilic aromatic substitution. In this intermediate (I) positive charges are located at carbons 2, 4, and 6. If we compare the *ortho*-substituted intermediate with the *para*-substituted intermediate (II) we see that the substituent in each case is adjacent to one charge and about the same distance from the other two. Thus the localized effect of the substituent should be the same in the *ortho*- and in the *para*-substituted intermediates as the geometry is essentially the same. The transition-state structure will resemble to some extent the structure of the intermediate. Therefore it is not unreasonable to assume that the *ortho* and *para* transition states will have the same geometry and will exhibit the same localized effect.



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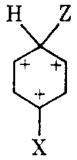

II

The Delocalized Electrical Effect.—For purposes of comparison values of β_o have been correlated with values of β_p. The results of the correlation are presented in Table III. The results show that β_o is $= 0.77\beta_p$; that is, the effect of resonance upon *ortho* substitution is somewhat less than that upon *para* substitution. This result is in accord with arguments presented by Norman and Radda[7] to the effect that the *para*-substituted intermediate is stabilized to a greater extent by resonance than is the *ortho*-substituted intermediate.

Composition of the *ortho* Electrical Effect.—We find it conventient to describe the composition of the elec-

[7] R. D. C. Norman and G. K. Radda, *J. Chem. Soc.*, 3610 (1961).

TABLE I

PARTIAL RATE FACTORS FOR ELECTROPHILIC AROMATIC SUBSTITUTION

Set	Reaction	Reagent	Solvent	Ref
1	Detritiation	H_2SO_4	$CF_3CO_2H-H_2O$	*a*
2	Nitration	HNO_3	$MeNO_2$	*a*
3	Nitration	NO_2BF_4	$C_4H_8SO_2$	*a*
4	Nitration	$AcONO_2$	Am_2O	*a*
5	Chlorination	Cl_2	AcOH	*a*
6	Chlorination	$Cl_2 + FeCl_3$	$MeNO_2$	*b*
7	Chlorination	$Cl_2 + AlCl_3$	$MeNO_2$	*b*
8	Bromination	Br_2	$AcOH-H_2O$	*a*
9	Bromination	$Br_2(l) + FeCl_3$	$MeNO_2$	*c*
10	Bromination	Br_2 in $MeNO_2 + FeCl_3$	$MeNO_2$	*c*
11	Bromination	$(Br_2 + FeCl_3)$ in $MeNO_2$	$MeNO_2$	*c*
12	Mercuration	$Hg(OAc)_2$	AcOH	*a, d*
13	Mercuration	$Hg(OAc)_2$	AcOH	*a*
14	Mercuration	$Hg(O_2CCF_3)_2$	CF_3CO_2H	*e*
15	Benzylation	$PhCH_2Cl + AlCl_3$	$MeNO_2$	*a*
16	Ethylation	$EtBr + GaBr_3$	$C_2H_4Cl_2$	*a*
17	Isopropylation	$MeCH{=}CH_2 + AlCl_3$	$MeNO_2$	*f*
18	Isopropylation	*i*-PrBr + $AlCl_3$	$MeNO_2$	*f*
19	Isopropylation	*i*-PrBr + $FeCl_3$	$MeNO_2$	*f*

		ortho partial rate factors									
Set	X = F	Cl	Br	I	Me	Et	*i*-Pr	Ph	NHAc	OMe	OPh
01	0.13	0.035	0.027	0.043	541	133					
02		0.0277	0.030	0.253	38.9						
03	0.115	0.093	0.093	0.304	3.2						
04	0.037				46.5	31.4	14.8	41			117
05	0.22	0.097	0.084		617	450	218	190	6.1×10^5	6.1×10^6	
06	0.222	0.217	0.201		27.5	20.0					
07	0.254	0.236	0.197		34.7						
08					600	465	180	37.5		8.7×10^7	
09	0.217	0.213	0.212		4.46	4.02					
010	0.0851	0.0796	0.0780		15.1						
011	0.171	0.151	0.131		7.42						
012	0.53	0.081	0.068		3.51			0.221			
013	0.63	0.075	0.070		5.71			0.0813		186	
014	0.0983	0.0168	0.0126		3.62	1.96	0.533				
015	0.203	0.248	0.175	0.256	4.20	3.12					
016	0.364	0.271	0.096		2.84			0.905			
017	0.285	0.177	0.116		2.70						
018	0.343	0.200	0.171		2.84						
019	0.288	0.149	0.123		2.97						

		meta partial rate factors								
Set	X = F	Cl	Br	I	Me	Et	*i*-Pr	*t*-Bu	Ph	OMe
m1	0.002	0.002	0.001	0.003	9.2			32		
m2		0.00084	0.00098	0.0112	1.3			3.7		
m3		0.0029	0.0040		0.14			0.38		
m4										
m5	0.0056	0.0023	0.0032		4.95			6.0	0.74	
m6	0.0174	0.0158	0.0144		0.932	0.893				
m7	0.0245	0.0205	0.0135		1.10					
m8	0.0010	0.00056	0.00053		5.5			6.09	0.3	2.0
m12	0.109	0.058	0.062		1.70			2.58	0.681	
m13	0.040	0.060	0.054		2.23			3.41	0.773	1.2
m14	0.00687	0.00820	0.00954		2.55	2.37	2.18	1.97		
m15		0.0043	0.0038	0.0059	0.43	0.37				
m16	0.116	0.102	0.087		1.56				0.695	
m17	0.0145	0.0168	0.0181		0.888					
m18	0.0131	0.0237	0.0271		0.895					
m19	0.0235	0.0316	0.0383		1.03					

		para partial rate factors											
Set	X = F	Cl	Br	I	Me	Et	*i*-Pr	*t*-Bu	Ph	NHAc	OPh	OMe	OH
p1	1.73	0.127	0.072	0.0865	702			863	143				
p2	0.77	0.130	0.103	0.776	45.8			71.6					
p3	2.47	0.643	0.526	1.07	3.2			5.3					
p4	0.77				48.5			57.7	38		2.30		
p5	3.93	0.406	0.310		820	840	650	401	590	2.52×10^6		4.6×10^7	
p6	1.26	0.555	0.470		24.2	29.6							
p7	1.48	0.627	0.480		38.2								

TABLE I (*Continued*)

Set	X = F	*para* partial rate factors											
		Cl	Br	I	Me	Et	*i*-Pr	*t*-Bu	Ph	NHAc	OPh	OMe	OH
p8	4.62	0.145	0.0618		2420	1800	1200	806	2920	1.2×10^9	1×10^8	1.1×10^{10}	3.7×10^{12}
p9	3.71	1.67	1.38		4.64	6.13							
p10	1.45	0.561	0.444		11.6								
p11	2.54	0.899	0.699		6.37								
p12	1.87	0.26	0.22		11.2			9.61	4.02		1.94	2310	
p13	2.98	0.36	0.27		23.0			17.2	6.42	277			
p14	1.51	0.232	0.194		46.9	42.8	39.0	32.3					
p15		0.955	0.721	1.15	10.0	7.7							
p16	0.738	0.588	0.433		6.02				2.23				
p17	0.778	0.271	0.151		4.56								
p18	0.777	0.254	0.179		4.70								
p19	0.948	0.315	0.242		5.26								

[a] Reference 1. [b] G. A. Olah, S. J. Kuhn, and B. A. Hardie, *J. Amer. Chem. Soc.*, **86**, 1055 (1964). [c] G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *ibid.*, **86**, 1039, 1044 (1964). [d] At 90°. [e] H. C. Brown and R. A. Wirkkala, *ibid.*, **88**, 1456 (1966). [f] G. A. Olah, S. H. Flood, and M. E. Moffat, *ibid.*, **86**, 1065 (1964); G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffat, and N. A. Overchuck, *ibid.*, **86**, 1046 (1964).

TABLE II

RESULTS OF CORRELATIONS WITH EQ 1

Set	*ortho* partial rate factors								
	$-\alpha$	$-\beta$	h	R[a]	F[b]	r[c]	s_{estd}[d]	s_α[d]	s_β[d]
01	9.93	4.75	2.04	0.987	56.59	0.675	0.406	1.06	1.84
02	5.00	−5.20	1.96	0.999	222.8	0.680	0.121	0.388	1.49
03	2.82	0.174	0.360	0.975	18.93	0.612	0.207	0.566	0.944
03A	3.29	1.27	0.188	0.9998	1041	0.729	0.0286	0.0906	0.169
04	9.68	8.91	0.379	0.772	2.214	0.934	1.04	5.26	6.58
04A	1.67	1.86	−1.31	0.999	186.3	0.952	0.144	0.919	1.21
05	12.3	15.5	1.11	0.794	5.121	0.649	1.98	3.96	5.91
05A	12.7	15.1	0.838	0.922	14.16	0.646	1.22	2.44	3.63
06	4.33	1.30	1.01	0.999	462.1	0.805	0.0736	0.213	0.433
07	4.66	1.55	1.12	0.999	180.0	0.729	0.0996	0.315	0.586
08	6.71	18.0	−1.75	0.996	125.1	0.875	0.322	2.54	1.83
09	2.73	0.769	0.405	0.9997	1545	0.805	0.0255	0.0739	0.150
010	4.78	1.41	0.770	0.9996	662.5	0.729	0.0540	0.171	0.318
011	3.67	1.35	0.524	0.999	183.6	0.729	0.0766	0.242	0.451
012	4.19	5.42	−0.525	0.959	11.54	0.784	0.279	0.879	1.60
013	5.33	8.21	−0.829	0.957	16.19	0.511	0.518	1.17	1.56
014	5.66	5.16	−0.426	0.998	230.3	0.805	0.106	0.308	0.626
015	2.62	0.731	0.346	0.994	120.2	0.687	0.0909	0.211	0.413
016	2.95	2.43	−0.00169	0.956	10.52	0.784	0.232	0.729	1.32
017	2.95	2.10	0.0283	0.991	26.40	0.729	0.144	0.455	0.846
018	2.73	1.90	0.0877	0.998	131.6	0.729	0.0601	0.190	0.354
019	3.12	2.26	0.0444	0.998	119.4	0.729	0.0711	0.225	0.419

Set	s_{h}[d]	n[e]	C.L.$_{\text{reg}}$[f]	t_α[g]	C.L.$_\alpha$[f]	t_β[g]	C.L.$_\beta$[f]	t_{h}[g]	C.L.$_{\text{h}}$[f]
01	0.339	6	99.5	9.368	99.0	2.582	90.0	6.017	99.0
02	0.208	4	...[h]	12.89	95.0	3.490	80.0	9.420	90.0
03	0.208	5	90.0	4.982	95.0	0.1843	20.0	1.731	50.0
03A	0.0332	4	97.5	36.31	98.0	7.515	90.0	5.662	80.0
04	0.997	6	90.0	1.840	80.0	1.354	50.0	3.801	95.0
04A	0.211	4	90.0	1.817	50.0	1.537	50.0	6.209	80.0
05	1.27	9	90.0	3.106	95.0	2.623	95.0	0.8740	50.0
05A	0.785	8	99.5	5.205	99.0	4.160	99.0	1.068	50.0
06	0.0708	5	99.5	20.33	99.0	3.002	90.0	14.27	99.9
07	1.16	4	90.0	14.79	95.0	2.645	50.0	0.9655	20.0
08	0.299	5	99.0	2.642	80.0	9.836	98.0	5.853	95.0
09	0.0246	5	99.9	36.94	99.9	5.127	95.0	16.46	99.0
010	0.0627	4	95.0	27.95	95.0	4.434	80.0	12.28	90.0
011	0.0889	4	90.0	15.17	95.0	2.993	50.0	5.894	80.0
012	0.261	5	90.0	4.767	95.0	3.388	90.0	2.011	80.0
013	0.445	6	97.5	4.556	98.0	5.263	98.0	1.863	80.0
014	0.102	4	95.0	18.38	95.0	8.243	90.0	4.176	80.0
015	0.0732	6	99.5	12.42	99.0	1.770	80.0	5.726	98.0
016	0.216	5	90.0	4.046	90.0	1.841	50.0	0.0078	20.0
017	0.167	4	90.0	6.484	90.0	2.482	50.0	0.0169	20.0
018	0.0697	4	90.0	14.37	95.0	5.363	80.0	1.258	50.0
019	0.0826	4	90.0	13.87	95.0	4.394	80.0	0.5375	20.0

TABLE II (*Continued*)

	meta partial rate factors									
Set	$-\alpha$	$-\beta$	h	R^a	F^b	r^c	s_{estd}^d	s_α^d	s_β^d	s_h^d
m1	8.41	2.84	0.378	0.997	216.0	0.649	0.221	0.480	0.990	0.185
m2	5.27	−6.03	0.784	0.996	118.8	0.712	0.222	0.578	2.68	0.374
m2A	9.00	12.3	−1.73	0.9991	284.1	0.990	0.142	1.93	9.48	1.30
m3	5.32	8.84	−2.06	0.993	33.62	0.490	0.225	3.05	15.0	2.06
m5	6.91	2.69	0.0549	0.997	289.0	0.793	0.151	0.405	0.836	0.133
m6	3.79	1.28	−0.371	0.9994	897.6	0.805	0.0455	0.132	0.268	0.0438
m7	3.96	1.81	−0.377	0.995	46.40	0.729	0.159	0.503	0.936	0.185
m8	9.15	5.18	−0.324	0.995	199.9	0.586	0.234	0.472	0.705	0.172
m12	3.37	1.91	−0.0985	0.998	441.9	0.793	0.0555	0.149	0.307	0.0489
m13	3.80	1.58	0.0657	0.989	88.97	0.586	0.151	0.305	0.455	0.111
m14	4.83	0.661	0.0313	0.998	540.9	0.834	0.0972	0.253	0.564	0.0868
m15	4.22	1.37	−0.761	0.9992	638.2	0.777	0.0596	0.176	0.730	0.0918
m16	2.64	1.04	−0.0417	0.997	188.9	0.784	0.0585	0.184	0.334	0.0547
m17	3.47	0.561	−0.293	0.99993	3,396	0.729	0.0182	0.0577	0.107	0.0212
m18	2.93	−0.479	−0.137	0.99999	20,325	0.729	0.00716	0.0227	0.0422	0.00831
m19	2.89	−0.00709	−0.132	0.99990	2,627	0.729	0.0184	0.0582	0.108	0.0213

Set	n^e	C.L.$_{\text{reg}}^f$	t_α^g	C.L.$_\alpha^f$	t_β^g	C.L.$_\beta^f$	t_h^g	C.L.$_h^f$
m1	6	99.9	17.52	99.9	2.868	90.0	2.043	80.0
m2	5	n.s.[h]	9.117	98.0	2.250	80.0	2.096	80.0
m2A	4	95.0	4.663	80.0	1.297	50.0	1.331	50.0
m3	4	90.0	1.744	50.0	0.5893	20.0	1.000	50.0
m5	6	99.9	13.96	99.9	3.218	95.0	0.4128	20.0
m6	5	99.5	28.71	99.9	4.776	95.0	8.470	98.0
m7	4	90.0	7.872	90.0	1.934	50.0	2.038	50.0
m8	7	99.9	19.39	99.9	7.347	99.0	1.884	80.0
m12	6	99.9	22.62	99.9	6.221	99.0	2.014	80.0
m13	7	99.9	12.46	99.9	3.473	95.0	0.5919	20.0
m14	7	99.9	19.09	99.9	1.172	50.0	0.3606	20.0
m15	5	99.5	23.98	99.0	1.876	50.0	8.290	98.0
m16	5	99.0	14.35	99.0	3.114	90.0	0.7623	20.0
m17	4	97.5	60.13	98.0	5.243	80.0	13.82	95.0
m18	4	n.s.[h]	129.1	99.0	11.35	90.0	16.48	95.0
m19	4	97.5	49.65	98.0	0.0756	20.0	6.197	80.0

	para partial rate factors									
Set	$-\alpha$	$-\beta$	h	R^a	F^b	r^c	s_{estd}^d	s_α^d	s_β^d	s_h^d
p1	9.02	6.81	1.70	0.987	73.48	0.678	0.373	0.807	1.64	0.280
p2	5.18	2.75	1.12	0.970	23.93	0.649	0.388	0.842	1.74	0.325
p2A	6.24	5.24	0.728	0.9995	996.6	0.780	0.0613	0.165	0.358	0.0630
p3	1.81	2.16	0.248	0.923	8.661	0.649	0.201	0.436	0.899	0.168
p3A	2.33	3.39	0.0525	0.992	64.93	0.780	0.0771	0.208	0.450	0.0792
p4	6.61	6.84	0.785	0.780	1.555	0.417	0.821	3.89	4.98	0.846
p4A	11.2	14.0	−0.693	0.994	39.89	0.951	0.206	1.28	1.79	0.341
p5	10.9	16.7	−0.0348	0.782	5.512	0.672	1.86	3.54	5.56	1.13
p5A	11.7	17.6	−0.677	0.939	18.69	0.665	1.06	2.03	3.29	0.711
p6	4.00	2.72	0.926	0.998	209.7	0.805	0.0863	0.250	0.508	0.0831
p7	4.26	3.01	0.101	0.998	114.6	0.729	0.0999	0.316	0.588	0.116
p8	14.7	24.7	0.505	0.862	13.06	0.608	2.46	4.21	4.86	1.32
p8A	16.2	25.8	−0.0545	0.953	39.41	0.613	1.48	2.55	2.94	0.804
p9	1.54	2.05	0.423	0.975	19.18	0.805	0.0889	0.259	0.524	0.856
p10	3.30	2.90	0.550	0.998	103.0	0.729	0.0777	0.246	0.458	0.0902
p11	2.39	2.84	0.342	0.996	57.41	0.729	0.0710	0.225	0.418	0.0824
p12	4.05	4.41	0.295	0.983	42.62	0.793	0.179	0.479	0.989	0.157
p13	5.57	8.08	0.324	0.890	11.38	0.603	0.696	1.39	1.81	0.480
p13A	5.75	8.28	0.133	0.973	45.22	0.604	0.358	0.715	0.930	0.251
p14	5.49	4.92	0.743	0.993	144.3	0.834	0.158	0.410	0.916	0.141
p15	2.07	3.56	0.801	0.992	61.56	0.777	0.0968	0.287	1.19	0.149
p15A	3.77	7.49	−0.0701	0.9992	295.8	0.989	0.0424	0.567	2.38	0.291
p16	2.39	1.44	0.463	0.992	65.06	0.784	0.0825	0.260	0.471	0.0771
p17	3.40	3.48	0.0672	0.987	19.31	0.729	0.179	0.566	1.05	0.208
p18	3.35	3.35	0.100	0.995	52.22	0.729	0.108	0.341	0.635	0.125
p19	3.19	3.18	0.178	0.997	81.32	0.729	0.0822	0.260	0.484	0.0955

	X							
Set	n^e	C.L.$_{\text{reg}}^f$	t_α^g	C.L.$_\alpha^f$	t_β^g	C.L.$_\beta^f$	t_h	C.L.$_h^f$
p1	7	99.9	11.18	99.9	4.152	98.0	6.071	99.0
p2	6	97.5	6.152	99.0	1.580	50.0	3.446	95.0
p2A	5	99.5	37.82	99.9	14.64	99.0	11.56	99.0
p3	6	90.0	4.151	95.0	2.403	90.0	1.476	50.0

TABLE II (*Continued*)

	X							
Set	n^e	$\text{C.L.}_{\text{reg}}{}^f$	$t_\alpha{}^g$	$\text{C.L.}_\alpha{}^f$	$t_\beta{}^g$	$\text{C.L.}_\beta{}^f$	t_h	$\text{C.L.}^f{}_\text{h}$
p3A	5	97.5	11.20	99.0	7.533	98.0	0.6629	20.0
p4	5	90.0	1.699	50.0	1.373	50.0	0.9279	50.0
p4A	4	90.0	8.750	90.0	7.821	90.0	2.032	50.0
p5	10	90.0	3.079	98.0	3.003	98.0	0.0308	20.0
p5A	8	99.5	5.764	99.0	5.350	99.0	0.9521	50.0
p6	5	99.5	16.00	99.0	5.354	95.0	11.14	99.0
p7	4	90.0	13.48	95.0	5.119	80.0	8.707	90.0
p8	12	99.0	3.492	99.0	5.082	99.9	0.3826	20.0
p8A	11	99.9	6.352	99.9	8.775	99.9	0.0068	20.0
p9	5	95.0	5.946	95.0	3.912	90.0	4.942	90.0
p10	4	90.0	13.41	95.0	6.332	90.0	6.098	80.0
p11	4	90.0	10.62	90.0	6.794	90.0	4.150	80.0
p12	6	99.0	8.455	99.0	4.459	95.0	1.879	80.0
p13	9	99.9	4.007	99.0	5.464	99.0	0.6750	20.0
p13A	8	99.9	8.042	99.9	8.903	99.9	0.5299	20.0
p14	7	99.9	13.39	99.9	5.371	99.0	5.270	99.0
p15	5	97.5	7.213	99.0	2.992	90.0	5.376	98.0
p15A	4	95.0	6.649	90.0	3.147	80.0	0.2401	20.0
p16	5	97.5	9.192	98.0	3.057	90.0	6.005	95.0
p17	4	90.0	6.007	80.0	3.314	80.0	0.3231	80.0
p18	4	90.0	9.824	90.0	5.275	80.0	0.800	20.0
p19	4	90.0	12.27	90.0	6.570	90.0	1.864	50.0

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficient of σ_I on σ_R. [d] Standard errors of the estimate, α, β, and h. [e] Number of points in set. [f] Confidence levels for regression, α, β, and h. [g] "t" test for significance of α, β, and h. [h] Not significant owing to difference in sign of α and β.

trical effect in terms of the ratio of β to α. Thus

$$\epsilon = \beta/\alpha \tag{21}$$

Then, for *ortho* substitution we may write

$$\epsilon_o = \beta_o/\alpha_o \tag{22}$$

From the correlation of α_o with α_p we obtain $\alpha_o = \alpha_p$. From the correlation of β_o with β_p we obtain $\beta_o = 0.77\beta_p$. Then

$$\epsilon_0 = \frac{0.77\beta_p}{\alpha_p} = 0.77\epsilon_p \tag{23}$$

Table III

CORRELATION OF α_o WITH α_p AND β_o WITH β_p

	m^a	c^b	r^c	s^d	$s_\text{m}{}^d$	t^e	C.L.[f]	n^g
A	1.00	0.515	0.976	0.643	0.0620	16.17	99.9	15
B	0.767	−0.139	0.967	1.37	0.0543	14.13	99.9	16

[a] Slope. [b] Intercept. [c] Correlation coefficient. [d] Standard error of the estimate and of m. [e] "t" test for significance of m (and of regression). [f] Confidence level for significance of regression. [g] Number of points in the set.

For those sets of *para* partial rate factors studied here in which β was significant we find an average value ϵ_p of 1.15. Exclusion of those sets in which the value

TABLE IV[a]

VALUES OF THE RATIO $p_o/2p_p$

Set	F	Cl	Br	I	Me	Et	*i*-Pr	Ph	NHAc	OMe	NO_2	CN	CHO	CF_3
R2	0.0476	0.213	0.292	0.321	0.848					0.407	10.7[d]	4.28[d]	1.06[d]	
R3	0.0464	0.144	0.176	0.285	1.03									
R4	0.0476				0.934	0.452	0.207			0.500				
R5	0.0612	0.240	0.414		0.753	0.531	0.333	0.564	0.241	0.133				
R6	0.176	0.391	0.427		1.13	0.673								
R7	0.171	0.376	0.410		0.908									
R8					0.246	0.255	0.149	0.0128		0.00813				
R9	0.0556	0.127	0.154		0.961	0.655								
R10	0.0556	0.142	0.176		1.30									
R11	0.0675	0.168	0.187		1.16									
R12	0.284	0.310	0.307		0.314			0.0551						
R14	0.0649	0.0723	0.0651		0.0772	0.0457	0.0137							
R15	0.0864	0.248	0.293	0.183	0.418	0.403								
R16	0.499	0.504	0.221		0.473			0.405						
R17	0.366	0.657	0.769		0.594									
R18	0.371	0.589	0.689		0.605									
R19	0.362	0.635	0.708		0.564									
R20[b]		0.292	0.349		1.62					0.268	5.87	4.00	2.65	1.96
R21[c]	0.0618	0.141			0.269									

[a] Set numbers refer to Table I unless otherwise noted. Data are from Table I unless otherwise noted. [b] $Cl_2/CCl_4/HClO_4/AgClO_4/25°$ (ref 7). [c] $(3\text{-}O_2NC_6H_4SO_2O)_2$ in PhX at room temperature: R. L. Dannley and G. E. Corbett, *J. Org. Chem.*, **31**, 153 (1966). [d] Reference 7.

TABLE V

RESULTS OF CORRELATIONS WITH EQ 29

Set	β'	h	r	t	s	n	n	C.L.
R2	2.48	0.191	0.800	3.528	0.453	0.702	9	99.0
R2A	4.02	0.359	0.968	8.605	0.222	0.468	7	99.9
R3	3.13	0.0344	0.891	3.392	0.257	0.924	5	95.0
R4	1.25	−0.142	0.498	1.148	0.485	1.09	6	50.0
R4A	3.40	0.254	0.955	4.535	0.228	0.751	4	95.0
R5	1.96	−0.0639	0.894	5.276	0.164	0.372	9	99.0
R5A	2.10	−0.00656	0.917	5.614	0.158	0.374	8	99.0
R6	1.96	0.116	0.935	4.584	0.122	0.427	5	98.0
R7	2.01	0.116	0.970	5.602	0.0889	0.358	4	95.0
R8	2.71	−0.677	0.677	1.593	0.620	1.70	5	50.0
R8A	3.63	−0.203	0.9995	30.14	0.403	0.120	3	95.0
R9	3.29	0.117	0.911	3.837	0.246	0.857	5	95.0
R10	3.57	0.242	0.888	2.732	0.324	1.31	4	80.0
R11	3.22	0.186	0.893	2.800	0.286	1.15	4	80.0
R12	−1.01	−0.899	0.431	0.827	0.346	1.23	5	50.0
R12A	0.122	−0.483	0.973	5.910	0.00560	0.0226	4	95.0
R14	−0.786	−1.47	0.375	0.808	0.295	0.973	6	50.0
R15	1.59	−0.298	0.855	3.300	0.146	0.483	6	95.0
R15A	1.92	−0.173	0.996	18.36	0.0300	0.105	5	99.9
R16	−0.201	−0.442	0.189	0.333	0.170	0.603	5	20.0
R17	0.770	−0.0397	0.794	1.844	0.104	0.417	4	50.0
R18	0.722	−0.0723	0.881	2.635	0.0680	0.274	4	80.0
R19	0.706	−0.0757	0.791	1.831	0.0957	0.386	4	50.0
R20	2.10	0.280	0.889	4.760	0.265	0.440	8	99.0
R20A	3.30	0.345	0.958	6.644	0.177	0.497	6	99.0
R21	1.85	−0.372	0.995	10.16	0.0443	0.182	3	90.0

of h was significant gives an average value of ϵ_p of 1.27.

The *ortho–para* Ratio in Electrophilic Aromatic Substitution.—From the definition of partial rate factors we may write

$$f_X{}^o = \frac{k_{PhX} \times 6 \times p_o}{k_{PhH} \times 2 \times 100} \qquad (24)$$

where p_o is per cent *ortho* substitution and k_{PhX} and k_{PhH} are rate constants for the substituted benzene and benzene itself. Similarly

$$f_X{}^p = \frac{k_{PhX} \times 6 \times p_p}{k_{PhH} \times 100} \qquad (25)$$

From eq 1 we may write

$$\log f_X{}^o = \alpha_o\sigma_{I,X} + \beta_o\sigma_{R,X} + h_o \qquad (26)$$

$$\log f_X{}^p = \alpha_p\sigma_{I,X} + \beta_p\sigma_{R,X} + h_p \qquad (27)$$

Then

$$\log\left(\frac{f_X{}^o}{f_X{}^p}\right) = \log\left(\frac{p_o}{2p_p}\right)_X = (\alpha_o - \alpha_p)\sigma_{I,X} + (\beta_o - \beta_p)\sigma_{R,X} + (h_o - h_p) \qquad (28)$$

Now as $\alpha_o = \alpha_p$ and $\beta_o = 0.77\beta_p$ we write

$$\log\left(\frac{p_o}{2p_p}\right)_X = -0.23\beta_p\sigma_{R,X} + h' = \beta'\sigma_{R,X} + h' \qquad (29)$$

where $h' = h_o - h_p$. In the general case h' will equal zero.

To provide a test of eq 29 we have correlated it with all of the available data. The data used are set forth in Table IV. The results of these correlations are given in Table V. The results for set R2 were significantly improved by the exclusion of the value for X = OMe and CHO (set R2A). Significant correlation was obtained for set R4 on the exclusion of X = OPh and *i*-Pr (set R4A) and set R8 on the exclusion of X = Ph and *i*-Pr (set R8A). As set 8A has only three points, two of which are alkyl groups, its value is doubtful. Exclusion of the point for X = Ph (set R12A) gave a significant correlation for set 12. Exclusion of the value for X = I from set R15 gave an excellent correlation (set R15A). Elimination of the points for X = CF_3 and X = OMe (set R20A) gave some improvement in the correlation for the set R20. It is noteworthy that the values of h' are not significantly different from zero.

Of 19 sets studied 12 gave significant correlation. All of the sets with eight or more members gave excellent correlation. We believe that, although the results are not absolutely certain, they do tend to support the validity of eq 29.

Steric Effects of *ortho* Substituents.—For most of the substituents studied, the substituent effect can be accounted for in terms of electrical effects as noted above. Certain substituents consistently (or often) show deviations suggestive of steric effects. These substituents include *t*-Bu, *i*-Pr, CF_3, I, and occasionally Ph.

Preformed Substituting Reagents.—Of the 19 sets studied in this paper eight are based on the work of Olah, *et al.*,[8] who have used the so-called preformed substitution reagents. A referee has pointed out that this work has been criticized as the relative rates

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[8] Table I, footnotes *b*, *c*, and *f*.

and thus the partial rate factors may be controlled by the rate of mixing and diffusion of the reagents. If this were indeed the case we would expect no correlations for Olah's data or at the very least entirely different behavior for these sets. This is apparently not the case. There seems to be no difference in behavior between Olah's data and the other sets studied.

Variation of *ortho* Substitution with Reagent.—Equation 29 predicts that for a constant substrate, *e.g.*, toluene

$$\log\left(\frac{p_o}{2p_p}\right)^X = m'\beta_p + h' \qquad (30)$$

where

$$m' = -0.23\sigma_{R.X} \qquad (31)$$

Thus the variation of the *ortho–para* ratio with reagent should be a linear function of β_p for any given substrate. Equation 30 does not seem to be obeyed. We may perhaps account for this at least in part in terms of a steric effect of the reagent which is constant throughout a set of substituted benzenes but varies from one reagent to another. The small value of m' expected for most substituents suggests that the predominant effect of the reagent may well be steric.

Cyclopropylcarbinyl 3,5-Dinitrobenzoate Solvolysis. 1-Ring Substituent Effect Study

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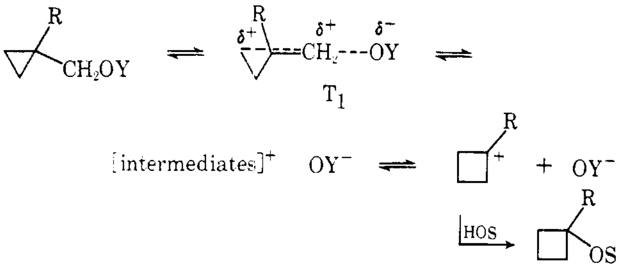
The solvolysis rates of the 3,5-dinitrobenzoate derivatives of cyclopropylcarbinol (**3**-H), 1-methylcyclopropylcarbinol (**3**-Me), 1-phenylcyclopropylcarbinol (**3**-Ph), 1-*p*-anisylcyclopropylcarbinol (**3**-An), cyclobutanol (**4**-H), 1-methylcyclobutanol (**4**-Me), and 1-phenylcyclobutanol (**4**-Ph) have been determined in 50 vol % aqueous dioxane. The relative first-order rates were found to parallel closely those for the acetolysis of the corresponding tosylate derivatives. The implications of this solvolytic behavior are discussed in terms of transition-state geometry and charge distribution.

In a recent paper,[1] a rationale was advanced explaining the insensitivity of the rate of solvolysis of cyclopropylcarbinyl tosylate to 1-ring substituents, in terms of a molecular reorganization mechanism (Scheme I) paralleling the solvolysis mechanism of similarly substituted allylcarbinyl tosylates. The lack of substituent effect upon solvolysis rate was attributed to a homoallyllike transition state, T_1, while the exclusive formation of ring expanded products was accommodated by a subsequent but greater structure reorganization, leading to a tertiarylike carbonium ion eventually captured by solvent.

SCHEME I



That a poorer leaving group in a solvolysis reaction will generate a transition state with less charge development but with greater orbital reorganization is a generally accepted postulate.[2] Furthermore, it is well established by the extensive work in the linear free-energy field[3] that substituent effects respond to variable charge development in classical S_N1-type reactions. On the other hand, there is increasing evidence[4] against a simple extension of substituent effects in classical ion formation to nonclassical ion formation. Accordingly, based upon the slight influence of γ substituents upon the reactivity of allylcarbinyl substrates,[4d] one would predict little substituent effect dependency upon leaving group in the solvolysis of 1-ring-substituted cyclopropylcarbinyl derivatives.

As a test of this thinking, the solvolytic behavior of seven cyclopropylcarbinyl 3,5-dinitrobenzoate derivatives was studied. The selection of leaving group was dictated by several considerations: (a) relative to tosylates, much more slowly ionizing 3,5-dinitrobenzoates would afford a more rigorous test of the proposed insensitivity of the transition state to 1-ring substituents; (b) high-purity substrates could be prepared with good room-temperature stability; and (c) *t*-cyclobutyl derivatives could be synthesized which would permit an assessment of the substituent effect upon the proposed intermediate capture by solvent.

Results and Discussion

The kinetic data are summarized in Table I. Each of the esters was allowed to solvolyze in 50 vol % aque-

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(1) D. D. Roberts, *J. Org. Chem.*, **33**, 2712 (1968).

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