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Nature of the *ortho* Effect. V. *ortho*-Substituent Constants

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Abstract: Thirty-two sets of *ortho*-substituent constants taken from the literature have been correlated with the equation $\sigma_{o,X} = \lambda\sigma_{I,X} + \delta\sigma_{R,X} + h$. The results show clearly that the *ortho*-substituent constants may be represented by the σ_I and σ_R constants and are independent of steric effects. They show further that the composition of the *ortho*-electrical effect cannot be represented by a single set of substituent constants. The composition of a substituent constant is represented by the expression $\epsilon = \delta/\lambda$. Values for ϵ for the *ortho*-substituent constants studied range from 0.2 to 1.4. The statement often quoted in the literature to the effect that in the absence of proximity effects the *ortho*- and *para*-electrical effects are the same is examined and shown to be incorrect. In the general case in the absence of proximity effects the *ortho*- and *para*-electrical effects must differ.

The definition of *ortho*-substituent constants is a problem which has received considerable attention over the last 15 years. At the present time, 32 sets of *ortho*-substituent constants have been defined. Generally, although not in all cases, they have been defined by means of the Hammett equation using the values of the slope ρ and intercept h obtained from a correlation of data for *meta*- and *para*-substituted compounds. Two problems arise in connection with these *ortho*-substituent constants: (1) do they represent only electrical effects (are steric effects absent?) and (2) is it possible to represent the *ortho*-electrical effect by a single set, or at most a few sets, of *ortho*-substituent constants? Another question of great interest arises from the often quoted statement that in the absence of proximity effects, the *ortho*-electrical effect should be of the same composition as the *para*-electrical effect.[1,2]

It is the purpose of this paper to attempt to answer these questions. In order to provide an answer to the first two questions, we have correlated all of the *ortho*-substituent constants which have been proposed so far with eq 1. This equation is based upon the Taft[3] separation of substituent effects into localized and delocalized contributions.

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

Successful correlation of the available *ortho*-substituent constants with eq 1 would be indicative of the absence of steric effects. If the *ortho* substituents are found to be a function solely of electrical effects, then a study of the variability of their composition defined as the ratio

$$\epsilon = \delta/\lambda \qquad (2)$$

will provide an answer to the second question. All of the available σ_o constants are gathered in Table I. These constants have been correlated with eq 1 by means of multiple linear regression analysis. The σ_I constants required are generally taken from our compilation.[4] The σ_R constants are obtained from the equation

$$\sigma_R = \sigma_p - \sigma_I \qquad (3)$$

the necessary σ_p constants being taken from the collection of McDaniel and Brown.[5]

The value for hydrogen has been excluded from the correlations for all sets for which it was available, as the unsubstituted compound has often been found to deviate from the correlation line obtained for *ortho*-substituted compounds. Substituents which are capable of intramolecular hydrogen bonding and the *t*-butyl group and other exceptionally bulky substituents were also excluded from the correlations.

The amino and dimethylamino substituents were excluded from the correlations of $E_{1/2}$ values of 2-substituted phenyl tosylates. The dimethylamino values are believed to be incorrect in dimethylformamide and in dimethyl sulfoxide, and both amino and dimethylamino values deviate for the *para*-substituted phenyl tosylates in acetonitrile.[6]

Results

Results of the correlations are presented in Table II. Of the 32 sets of *ortho*-substituent constants, 11 gave excellent correlations, 5 gave very good, 2 gave good, 3 gave fair, and 2 gave poor correlations. Nine sets did not give significant correlations with eq 1. All nine sets had only four points as did also both sets which gave poor results. It seems likely that had data been available better results would have been obtained. It is particularly pertinent in this regard that all of the sets with eight or more points gave excellent correlations.

Discussion

Steric Effects. The results of the correlations seem to show clearly that in general the *ortho*-substituent constants can be accounted for solely by the σ_I and σ_R constants. We conclude that the *ortho* effect is a pure electrical effect for most substituents. Obviously, the

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(1) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 206.

(2) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 593.

(3) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(4) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).

(5) D. H. McDaniel and H. C. Brown, *ibid.*, **23**, 420 (1958).

(6) V. M. Maremae, *Org. Reactivity*, **4**, 573 (1967).

Table I. *ortho*-Substituent Constants

1. Ionization of 2-Substituted benzoic acids[a]

X	Me	Et	*i*-Pr	Ph	CN	CO_2H	CO_2^-	$CONH_2$
σ_o	0.29	0.41	0.56	0.71	1.06[b]	0.95[b]	−0.91[b]	0.45[b]
X	NO_2	NH_3^+	OH	OMe	OEt	OPr	O-*i*-Pr	OPh
σ_o	1.99[b]	2.15[b]	1.22[b]	0.12	−0.01	−0.04	−0.04	0.67
X	OAc	F	Cl	Br	I			
σ_o	−0.37[b]	0.93	1.28	1.35	1.34			

2. Ionization of 2-substituted benzoic acids[c]

X	F	Cl	Br	I	Me
σ_o	0.53	0.83	0.91	0.84	−0.14

3. Ionization of 2-substituted anilinium ions[d]

X	Me	Et	*i*-Pr	NH_2	NH_3^+	NO_2	OH	OMe
σ_o	0.10	0.05	0.03	0	1.23[b]	1.72	−0.09	0
X	OEt	F	Cl	Br	I			
σ_o	0.02	0.47	0.67	0.71	0.70			

4. Ionization of 2-substituted phenols[a]

X	Me	Ph	OMe	CHO	*i*-Pr	*t*-Bu	CH_2OH	$CONH_2$
σ_o	−0.13	0	0	0.75	−0.23	−0.52[b]	0.04	0.72
X	F	Cl	Br	I	NO_2			
σ_o	0.54	0.68	0.70	0.63	1.24			

5. Ionization of 2-substituted phenols[e]

X	Me	Et	Ph	CH_2OH	MeO	CHO	F	Cl
σ_o	−0.13	−0.13	0	0.04	0.04	0.75	0.54	0.68
X	Br	I	NO_2	OH				
σ_o	0.70	0.63	1.40	0.04				

6. Ionization of 2-substituted phenylhydrazines[f]

X	OMe	OEt	Me	Cl	Br	CO_2H	NO_2
σ_o	−0.153	−0.143	−0.097	0.398	0.406	1.275	1.363

7. Ionization of 2-substituted phenylpropiolic acids[g]

X	Cl	NO_2	OMe	F	CF_3
σ_o	0.24	0.55	−0.13	0.13	0.21

8. Ionization of 2-substituted phenylpropiolic acids[g]

X	Cl	NO_2	F	CF_3
σ_o	0.21	0.48	0.27	0.25

9. Association of 2-substituted benzoic acids with diphenylguanidine[h]

X	NH_2	Me	Cl	NO_2
σ_o	−0.15	−0.15	0.38	1.00

10. Association of 2-substituted benzoic acids with diphenylguanidine[i]

X	H	F	Cl	Br	I	Me	NO_2
σ_o	0	0.51	0.82	0.91	0.96	−0.32	2.18

11. Detritiation of 2-substituted phenylacetylenes[j]

X	Br	Cl	Me	OMe
σ_o	0.56	0.57	−0.14	−0.33

12. Reaction of 2-substituted phenylpropiolic acids with diphenyldiazomethane[g]

X	Cl	NO_2	F	CF_3
σ_o	0.26	0.58	0.32	0.61

13. Reaction of 2-substituted phenylpropiolic acids with diphenyldiazomethane[g]

X	Cl	NO_2	F	CF_3
σ_o	0.27	0.57	0.27	0.35

14. Acid and alkaline hydrolysis of 2-substituted ethyl benzoates[k]

X	MeO	EtO	Me	H	F	Cl	Br	I	NO_2
σ_o	−0.39	−0.35	−0.17	0	0.24	0.20	0.21	0.21	0.80

15. Acid and alkaline hydrolysis of 2-substituted ethylbenzoates[l]

X	Me	Et	F	Cl	Br	I
σ_o	0.003	0.036	0.291	0.219	0.296	0.341

16. Alkaline hydrolysis of phenyl tosylates[m]

X	Me	CN	NO_2	OMe	F	Cl	Br	I	NH_2
σ_o	−0.191	1.080	1.247	−0.034	0.596	0.540	0.570	0.545	0.074

17. Alkaline fission of 2-substituted benzoyloxyethyldimethylsulfinium iodides[n]

X	NO_2	Cl	Me	OMe
σ_o	0.703	0.366	−0.054	−0.095

18. Vapor phase elimination in isopropyl benzoates[o]

X	OMe	Me	H	F	Cl	NO_2
σ_o	−0.53	−0.16	0	0.16	0.31	0.94

19. Partial rate factors for electrophilic aromatic substitution[p]

X	Me	EtO_2CCH_2	CH_2Cl	I	Br	Cl	CO_2Et
σ_o	−0.276	−0.112	0.0408	0.101	0.258	0.263	0.437

Table I (*Continued*)

20. $E_{1/2}$ for 2-substituted phenyl tosylates in dimethylformamide[a]									
X	F	Cl	NH_2	MeO	Me	NMe_2			
σ_o	0.546	0.517	0.011^b	−0.042	0.023	-1.879^b			
21. $E_{1/2}$ for 2-substituted phenyl tosylates in dimethyl sulfoxide[q]									
X	F	Cl	NH_2	OMe	Me	NMe_2			
σ_o	0.183	0.258	-0.047^b	−0.169	−0.029	-0.547^b			
22. $E_{1/2}$ for 2-substituted phenyl tosylates in acetonitrile[q]									
X	F	Cl	NH_2	OMe	Me	NMe_2			
σ_o	0.359	0.370	0.185^b	−0.179	−0.190	0.108^b			
23. $E_{1/2}$ for 2-substituted phenyl tosylates in pyridine[r]									
X	Cl	F	NH_2	NMe_2	OMe	Me			
σ_o	1.184	1.000	0.136^b	0.259^b	−0.221	−0.111			
24. $E_{1/2}$ for 2-substituted phenyl tosylates in benzonitrile[s]									
X	Cl	F	NH_2	NMe_2	OMe	Me			
σ_o	0.350	0.242	0.051^b	0.133^b	−0.100	−0.158			
25. $E_{1/2}$ for 2-substituted phenyl tosylates in pyridine–dimethylformamide[s]									
X	Cl	F	NH_2	NMe_2	OMe	Me			
σ_o	0.683	0.553	-0.089^b	0.016	−0.228	−0.049			
26. $E_{1/4}$ for 2-substituted phenylferrocenes[t]									
X	MeO	EtO	Me	H	F	Cl	Br	I	NO_2
σ_o	−0.39	−0.38	−0.03	0^b	0.12	0.31	0.34	0.36	0.79
X	CO_2H	CO_2Me	CH_2OH	Ph					
σ_o	0.23	0.29	0.09	−0.03					
27. Stretching frequencies of 2-substituted phenyl tosylates[u]									
X	NO_2	F	Cl	OMe	Me	NH_2			
σ_o	0.80	0.23	0.23	−0.05	−0.19	−0.33			
28. Stretching frequencies of 2-hydroxy-2-substituted benzanils[v]									
X	Cl	F	H	Me	MeO				
σ_o	0.22	0.17	0^b	−0.14	−0.34				
29. Stretching frequencies of 2-substituted benzonitriles[w]									
X	NH_2	OH	Me	Cl	NO_2				
σ_o	−0.35	−0.2	−0.1	0.4	0.95				
30. Hydroxyl chemical shifts of 2-substituted phenols[x]									
X	F	Cl	Br	I	CN	CF_3	Me	Et	Pr
σ_o	0.29	0.50	0.55	0.64	1.18	0.81	−0.13	−0.15	−0.16
X	*i*-Pr	*sec*-Bu	*t*-Bu	$EtMe_2C$	$BuCH_2CH_2$	$C_2H_8CH_2$	MeO_2CCHCH		
σ_o	−0.15	−0.18	−0.08	-0.15^b	−0.17	−0.07	0.62^b		
X	$PhCH_2$	CH_2OH	Ph	CHO	Bz	CO_2Me	CO_2CH_2Ph		
σ_o	−0.08	−0.07	0.21	1.02	0.93	0.88	0.86^b		
OAc	CONHPh	OH	OMe	OEt	AcNH	NMe_2	SMe	SOMe	
−0.01	0.79^b	−0.41	−0.37	−0.30	−0.08	−0.36	0.21	0.92	
31. Hydroxyl chemical shifts of 2-substituted phenols[x]									
X	Br	NO_2	Me	Pr	*i*-Pr	*sec*-Bu	*t*-Bu	$BuCH_2CH_2$	
σ_o	0.66	1.20	−0.03	−0.06	−0.03	−0.07	0	−0.08	
X	Ph	CHO	Ac	OMe					
σ_o	0.20	0.92	1.06	−0.23					
32. Amine chemical shifts of 2-substituted anilines[x]									
X	Cl	Br	Me	OMe	OEt				
σ_o	0.40	0.40	−0.17	−0.20	−0.23				

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[a] G. B. Barlin and D. D. Perrin, *Quart. Rev.* (London), **20,** 75 (1966). [b] Omitted from correlation. [c] A. Buckley, N. B. Chapman, and J. Shorter, *J. Chem. Soc., B*, 195 (1969). [d] J. Clark and D. D. Perrin, *Quart. Rev.* (London), **18,** 295 (1964). [e] P. J. Pearce and R. O. O. Simikins, *Can. J. Chem.*, **46,** 241 (1968). [f] G. Westphal and H. H. Stroh, *Z. Chem*,, **7,** 192 (1967). [g] I. J. Solomon and R. Filler, *J. Am. Chem. Soc.*, **85,** 3492 (1963). [h] M. M. Davis and H. B. Hetzer, *J. Res. Nat. Bur. Stand.*, **60,** 569 (1958). [i] C. L. Liotta, *Chem. Commun.*, 338 (1968). [j] C. Eaborn, G. A. Skinner, and D. R. M. Walton, *J. Chem. Soc.*, 922 (1966). [k] See ref 2, p 619. [l] N. B. Chapman, J. Shorter, and J. H. P. Utley, *J. Chem. Soc.*, 1291 (1963). [m] V. M. Maremae and J. R. Asenbush, *Org. Reactivity*, **2,** 83 (1965); V. M. Maremae, *ibid.*, **4,** 96 (1967). [n] P. Mamalis and H. N. Rydon, *J. Chem. Soc.*, 1049 (1955). [o] D. A. K. Jones and G. G. Smith, *J. Org. Chem.*, **29,** 3531 (1964). [p] C. W. McGary, Jr., Y. Okamoto, and H. C. Brown, *J. Am. Chem. Soc.*, **77,** 3037 (1955). [q] See ref 6. [r] V. M. Maremae, *Org. Reactivity*, **5,** 943 (1968). [s] V. M. Maremae, *ibid.*, **5,** 953 (1968). [t] W. F. Little, C. N. Reilley, J. D. Johnson, K. N. Lynn, and A. P. Sanders, *J. Am. Chem. Soc.*, **86,** 1376 (1964). [u] V. M. Maremae, *Org. Reactivity*, **4,** 87 (1967). [v] A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **81,** 1523 (1959). [w] H. W. Thompson and G. Steel, *Trans. Faraday Soc.*, **52,** 1451 (1956). [x] M. T. Tribble and J. G. Traynham, *J. Am. Chem. Soc.*, **91,** 379 (1969).

substituents which were excluded from the correlations due to bulk (*t*-butyl) or to intramolecular hydrogen bond formation (CO_2H, NH_3^+, etc., in the case of the 2-substituted benzoic acids) exert steric effects. *This is not the general case, however.*

Composition of the *ortho*-Substituent Constants. Values of ϵ are reported in Table III. The values obtained range from 0.2 to 1.4 with 15 of the 20 reliable values lying between $\epsilon = 0.50$ and $\epsilon = 1.0$. The results show that although correlation can usually be obtained

Table II. Results of Correlations with Equation 1

Set	λ	δ	h	R^a	F^b	r^c	$s_{\text{estd}}{}^d$	$s_\lambda{}^d$	$s_\delta{}^d$	$s_h{}^d$
1	2.43	2.50	0.775	0.969	69.56	0.505	0.138	0.231	0.253	0.0786
2	2.33	1.89	0.201	0.995	94.21	0.612	0.0631	0.172	0.287	0.0632
3	1.59	1.07	0.265	0.951	42.27	0.124	0.180	0.227	0.212	0.108
4	1.96	0.906	−0.0423	0.981	126.7	0.049	0.108	0.129	0.167	0.0502
5	1.86	0.822	−0.152	0.994	398.2	0.016	0.0554	0.0712	0.0742	0.0297
6	1.29	1.83	0.356	0.967	29.05	0.327	0.202	0.384	0.341	0.184
7	1.13	0.310	−0.265	0.986	35.06	0.554	0.0574	0.221	0.114	0.120
8	0.943	0.137	−0.174	0.987	19.38	0.181	0.0332	0.173	0.0695	0.0938
9	1.34	0.399	−0.0308	0.987	18.16	0.522	0.155	0.314	0.288	0.166
10	2.83	2.15	−0.0524	0.998	573.8	0.173	0.0580	0.0882	0.133	0.0404
11	1.77	1.80	0.165	0.99996	5813.0	0.224	0.00752	0.0185	0.0260	0.00868
12	0.125	0.559	0.444	0.897	2.059	0.181	0.136	0.711	0.286	0.385
13	0.892	0.296	−0.0655	0.998	119.4	0.181	0.0159	0.0826	0.0332	0.0448
14	1.15	1.02	−0.0695	0.975	47.24	0.257	0.103	0.184	0.183	0.100
15	0.607	0.300	0.0858	0.948	13.23	0.687	0.0593	0.137	0.269	0.0477
16	1.68	0.413	−0.0286	0.960	29.38	0.501	0.170	0.298	0.246	0.162
17	0.870	0.677	0.0684	0.995	52.17	0.390	0.0638	0.128	0.155	0.0694
18	1.09	1.45	0.121	0.975	19.38	0.195	0.168	0.303	0.338	0.171
19	1.22	0.983	−0.119	0.952	19.28	0.304	0.0908	0.200	0.328	0.0637
20	1.38	0.951	0.170	0.966	6.966	0.531	0.141	0.369	0.512	0.163
21	0.846	0.876	0.103	0.983	14.13	0.531	0.0626	0.164	0.228	0.0724
22	1.41	0.874	−0.0376	0.986	17.42	0.531	0.0917	0.291	0.334	0.106
23	3.30	2.47	0.309	0.992	30.40	0.531	0.161	0.423	0.587	0.186
24	1.13	0.715	−0.0140	0.9999	2569.0	0.531	0.00605	0.0159	0.0220	0.00699
25	1.99	1.72	0.226	0.987	18.83	0.531	0.124	0.326	0.452	0.144
26	0.963	0.931	0.00193	0.928	28.00	0.032	0.135	0.195	0.178	0.0799
27	1.08	0.550	−0.0576	0.991	80.21	0.405	0.0706	0.125	0.112	0.0718
28	1.13	1.14	0.0233	0.965	6.820	0.531	0.120	0.315	0.436	0.139
29	1.16	0.775	0.0579	0.996	115.2	0.498	0.0700	0.139	0.113	0.0740
30	1.54	1.17	0.0725	0.912	61.84	0.050	0.207	0.189	0.163	0.0725
31	1.47	1.52	0.209	0.985	147.7	0.249	0.0978	0.123	0.169	0.0398
32	1.37	1.19	0.0422	0.997	178.8	0.170	0.0347	0.0843	0.0968	0.0389

Set	n^e	C.L.^{f}	Set	n^e	C.L.^{f}	Set	n^e	C.L.^{f}
1	12	99.9	12	4	<90.0	23	4	<90.0
2	5	97.5	13	4	90.0	24	4	97.5
3	12	99.9	14	8	99.9	25	4	<90.0
4	13	99.9	15	6	95.0	26	12	99.9
5	12	99.9	16	8	99.5	27	6	99.5
6	7	99.0	17	4	90.0	28	4	<90.0
7	5	95.0	18	5	95.0	29	5	99.0
8	4	<90.0	19	7	99.0	30	28	99.9
9	4	<90.0	20	4	<90.0	31	12	99.9
10	7	99.9	21	4	<90.0	32	5	99.0
11	4	99.0	22	4	<90.0			

[a] Multiple correlation coefficient. [b] F test for significance of regression. Partial correlation coefficient of σ_I on σ_R. [d] Standard errors of the estimate, λ, δ, h. [e] Number of points in the set. [f] Confidence level for correlation.

Table III. Composition of the *ortho*-Substituent Constants

Set	ε	Set	ε	Set	ε
1	1.0	12		23	0.75[a]
2	0.81	13	0.33	24	0.63
3	0.68	14	0.89	25	0.86[a]
4	0.46	15	0.50	26	1.0
5	0.44	16	0.25	27	0.51
6	1.4	17	0.78	28	1.0[a]
7	0.27	18	1.3	29	0.67
8	0.15[a]	19	0.81	30	0.76
9	0.30[a]	20	0.69[a]	31	1.0
10	0.76	21	1.0[a]	32	0.87
11	1.0	22	0.62[a]		

[a] Correlation of this set was not significant. Value is approximate.

with σ_m (ϵ = 0.33), $\sigma_p{}^0$ (ϵ = 0.67), or σ_p (ϵ = 1.0), *no one set of ortho-substituent constants can be defined* which can be used for most *ortho*-substituent effect data. In our opinion, the most useful approach to the problem of the correlation of data for *ortho*-substituted benzene sets lies in the use of the extended Hammett equation.

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

Equation 4 has the advantage that the composition of the electrical effect is not specified, as it is in the simple Hammett equation by the choice of substituent constant.

The Relationship between the *ortho*- and *para*-Electrical Effects. Many authors have stated that in the absence of proximity effects the *ortho*-electrical effect ought to be the same as the *para*-electrical effect, that is, the *ortho*- and *para*-electrical effects should have the same magnitude and composition. The basis for this assumption seems to lie in the following statements by Hammett: "*ortho* substituents do not alter the entropy of activation of the aryl sulfuric acid hydrolysis and this reaction also shows no proximity effect. The effect of an *ortho* substituent is nearly the same as that of a *para* substituent, and the whole series of data closely parallels that obtained in the hydrolysis of cinnamic ester in which an *ortho* substituent is widely removed from the point of reaction," And "it is therefore very probable that the proximity effect acts through and is the direct result of the kinetic energy terms in the equilibrium and rate equations and that when, in special cases, these terms vanish for reaction in the *ortho* position *the rate of reaction in that position is nearly identical with that in the para position*." Statement 2 refers to electrophilic aromatic substitution. The concept of the sameness of the *ortho*- and *para*-electrical effects has been used by a number of authors[7,8] to justify the sets of *ortho*-substituent constants which they have proposed. It is therefore of the greatest importance to determine whether this concept is in fact justified.

There are two possible contributions to the localized effect—they are the field and the inductive effects. Let us consider each of these contributions in turn.

Consider a reaction used to define σ_o constants and σ_p constants. The data employed to define the substituent constants may also be represented by the extended Hammett equation. Then

$$Q_o = \alpha_o\sigma_{I,X} + \beta_o\sigma_{R,X} + h \tag{5}$$

$$= \rho_o\lambda_o\sigma_{I,X} + \rho_o\delta_o\sigma_{R,X} + h \tag{6}$$

Then

$$\alpha_o = \rho_o\lambda_o, \qquad \beta_o = \rho_o\delta_o \tag{7}$$

Similarly

$$\alpha_p = \rho_p\lambda_p, \qquad \beta_p = \rho_p\delta_p \tag{8}$$

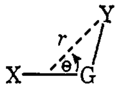
Now it has been shown that for any set of compounds XGY where X is a variable substituent, Y is the reaction site, and G is a skeletal group to which Y and Y are bonded

$$\alpha_G = \frac{\cos\theta_G\phi}{r^2_G} \tag{9}$$

where ϕ is given by

$$\phi = \frac{r^2_{G^0}}{\cos\theta_{G^0}}\alpha_{G^0} \tag{10}$$

G^0 referring to some reference group G. The angle θ and the distance r are defined in A



Thus

$$\alpha_o = \frac{\cos\theta_o}{r^2_o}\phi \quad \alpha_p = \frac{\cos\theta_p}{r^2_p}\phi \tag{11}$$

Now examination of the structures of the *ortho*- and *para*-substituted benzenes shows clearly that

$$r_o \neq r_p, \qquad \theta_o \neq \theta_p \tag{12}$$

Thus, except for the unusual case where by chance the differences in cos θ compensate for the differences in r^2, $\alpha_o \neq \alpha_p$ and therefore $\rho_o\lambda_o \neq \rho_p\lambda_p$. Now the definition of the σ_o constants requires that

$$\rho_o = \rho_p \tag{13}$$

Then

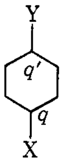
$$\lambda_o \neq \lambda_p \tag{14}$$

The inductive effect may be represented by the equation

$$\lambda = mq' \tag{15}$$

where q' is the charge induced by the substituent at the carbon to which the reaction site is bonded. This charge is given by the equation

$$q' = q\sum_i f^n \tag{16}$$



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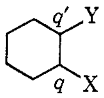

II

where q is the charge at the atom bearing the substituent X, f is the falloff factor, n is the number of carbon–carbon bonds between substituent and reaction site, and i is the number of paths joining substituent and reaction site. Using a value for the falloff factor[9] of 1/2.8 (0.357) we calculate

$$q_p' = 2f^3q = 0.089q \tag{17}$$

$$q_o' = (f + f^5)q = 0.363q \tag{18}$$

We conclude that according to the inductive effect

$$\lambda_o \neq \lambda_p \tag{14}$$

We may now turn to the delocalized effect. We have shown that

$$\beta = mq + c \tag{19}$$

where q is the π-electron density in the appropriate carbanion at the carbon bearing the reaction site. These values of q were calculated by the Dewar–Longuet-Higgins approximation method. Recently, Professor Paul Friedman[10] has communicated to us the results of SCF calculations on the benzyl carbanion according to which the values of q_o and q_p are -0.09687 and -0.144460. We conclude that

$$\beta_o \neq \beta_p \tag{20}$$

and therefore

$$\rho_o\delta_o \neq \rho_p\delta_p \tag{21}$$

From eq 13 it follows that

$$\delta_o \neq \delta_p \tag{22}$$

Thus in the absence of proximity effects the resonance effects at the *ortho* and *para* positions are decidedly different.

We conclude from this analysis of the *ortho*- and *para*-electrical effects that *only in an exceptional case is the ortho-electrical effect likely to have the same composition as the para-electrical effect.* In the general case, *ortho*- and *para*-electrical effects may be expected to differ in both magnitude and composition. In this regard it is of interest to note that of the 23 sets of *ortho*-

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(7) See Table I, footnote *l*.
(8) See Table I, footnote *x*.
(9) Reference 2, p 592.
(10) Department of Chemistry, Pratt Institute, Brooklyn, N. Y. 11205.

substituent constants which gave reliable correlations with eq 1, 17 have values of ϵ which are significantly different from the value for σ_p. Thus there is no special importance to be attached to those σ_o constants which do happen to have the same composition as the σ_p constants.

We hope that we have now laid to rest the assumption of equality between the *ortho*- and *para*-electrical effects.

The Temperature Variation of the H_0 Acidity Function in Aqueous Sulfuric Acid Solution

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Contribution from the School of Chemical Sciences, University of East Anglia, Norwich, England. *Received April 7, 1969*

Abstract: The variation of the H_0 acidity function, as defined by primary nitroaniline indicators, with temperature, has been examined by measurement of the scale at 25, 40, 60, 80, and 90°. Empirical equations correlating H_0 with temperature are deduced. The variation of pK_a values with temperature and the application of the scale to other measurements on acidity scales and acid-catalyzed reactions, at elevated temperatures, are discussed.

Many acid-catalyzed reactions have been reported in concentrated solutions of aqueous sulfuric acid at elevated temperatures. The H_0 values of such solutions relevant to the interpretation of such reactions have usually been assumed to be those of the solutions at room temperature. In particular, this assumption has been very commonly employed in recent and extensive investigations into the mechanism of aromatic and heteroaromatic nitration and hydrogen exchange;[1-3] however, it has become increasingly apparent that this assumption is a gross one, and this prompted us to accumulate accurate information on the effect of temperature on the H_0 scale.

Similar previous investigations have concerned aqueous solutions of phosphoric and hydrochloric acid,[4] and also sulfuric acid[5] (the latter indicated diagrammatically in Figure 1). We believe that the values reported for the study of sulfuric acid may be in error for several reasons. The indicators used by these workers were 4-nitro-, 2-nitro-, 4-chloro-2-nitro-, 2,4-dichloro-6-nitro-, 2,4-dinitro-, 2-bromo-4,6-dinitro-, and 2,4,6-trinitroaniline. Overlap between the third and fourth of these indicators necessitated measuring log I (log $[B]/[BH^+]$) values of up to -2.38; values of this magnitude are subject to large experimental uncertainty. Furthermore, there was no overlap at all between the fifth and sixth, and sixth and seventh of these indicators; the pK_a values of the latter two indicators were calculated by an extrapolation for which there is no theoretical justification.

The only other investigation of the temperature variation of an acidity function in aqueous sulfuric acid is that of H_R by Arnett and Bushick.[6]

Experimental Section

Materials. Sulfuric and hydrochloric acids were AnalaR grade reagents. Fuming sulfuric acid was prepared by distillation of sulfur trioxide into AnalaR grade sulfuric acid, using a process similar to that for the preparation of deuteriosulfuric acid.[7] Water was deionized and further purified by distillation from potassium permanganate in glass apparatus.

The nitroaniline indicators used, (1) 4-nitro-, (2) 2-nitro-, (3) 4-chloro-2-nitro-, (4) 2,5-dichloro-4-nitro-, (5) 2-chloro-6-nitro-, (6) 2,6-dichloro-4-nitro-, (7) 2,4-dinitro-, (8) 2,6-dinitro-, (9) 2-bromo-4,6-dinitro-, (10) 3-methyl-2,4,6-trinitro-, (11) 3-bromo-2,4,6-trinitro-, and (12) 2,4,6-trinitroaniline, were obtained commercially or made by standard procedures.[8] All were recrystallized several times from appropriate solvents and had accurate analyses and melting points which agreed with accepted literature values.

Preparation of Solutions. A stock acid solution was made by dilution of concentrated sulfuric acid with water, and estimated by titration with standard sodium hydroxide using screened methyl orange as indicator, or by adding an excess of potassium iodide–potassium iodate and titrating the liberated iodine against standard sodium thiosulfate using sodium starch glycollate as indicator. This stock acid solution was then diluted with water to give acids of the requisite strength; the procedure was carried out by weighing, and frequently checked by titration as above, agreement between the two results being well within experimental error. For more concentrated solutions, dilution of concentrated or fuming acid was employed.

The indicator stock solutions were prepared by addition of a weighed amount of the indicator to a volumetric flask and dissolving this in aqueous acid of sufficient strength to protonate it completely (to aid dissolution). A suitable volume of the stock solution was withdrawn by a micrometer syringe and added to standard acid (20 ml). The same operation was carried out using acids of the same strength, but without indicator present to yield a reference solution. All the above operations were checked by weighing.

Spectrophotometric Measurements. Two matched "UV grade" 1-cm cells (Unicam Instruments, Ltd., Cambridge, England) were filled with the indicator and reference solution, respectively, and closed with polyethylene stoppers (for measurements up to 60°) and with polypropylene stoppers (for higher temperatures). Absorbances were measured on a Unicam SP 500 spectrophotometer fitted with an electrically thermostated cell holder and controller (A. Adkins and Sons Ltd., Leicester, England). This cell holder was designed to take the two 1-cm cells, and was wired with 15 yards of Eureka 32 S. W. G. enamel-covered wire, half of it wound clockwise on one side of the block and half of it anticlockwise on

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[7] A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 239 (1946).

[8] For full details, see S. A. Shapiro, Ph.D. Thesis, University of East Anglia, 1969.