The Nature of the *ortho* Effect. III. Acid Hydrolysis of *ortho*-Substituted Benzoates and Esterification of *ortho*-Substituted Benzoic Acids

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Abstract: The effect of *ortho* substituents upon the rates of acid hydrolysis of methyl benzoates and upon the rates of acid-catalyzed esterification of benzoic acids is purely electrical in nature. Steric effects are unimportant. The electrical effect is almost entirely a resonance effect. The results provide conclusive proof for the proposal that the $E°_S$ constants are largely a measure of the resonance effect and do not in any way represent a steric effect.

We have previously shown[1] that the Taft $E°_S$ "steric" parameters[2] for *ortho* substituents which are defined from the acid-catalyzed esterification of *ortho*-substituted benzoic acids and/or the acid-catalyzed hydrolysis of *ortho*-substituted benzoates are a function of electrical effects and are independent of the van der Waals radii of the substituents. This behavior stands in sharp contrast to that of the E_S parameters which are linearly dependent on the van der Waals radii. Since many papers have appeared in the literature utilizing $E°_S$ values which were interpreted in terms of steric effects, it seemed of importance to investigate the nature of the *ortho* effect in the defining reaction. For this purpose we have correlated data taken from the literature with the equations

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

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \qquad (2)$$

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

Sets studied in the correlations are set forth in Table I.[3] Values of σ_I and σ_R are from the sources reported in the first papers of this series[1,4] as are the values of r_V. For substituents of the type YZ where Y is bonded to the ring and has a lone pair (*e.g.*, OMe, NH_2), the r_V value of Y was used in the correlation. For the Me group the minimum perpendicular van der Waals radius was used.

The van der Waals parameter for the nitro group was taken to be the sum of the distance from the O–N–O angle bisector to one of the O atoms and the van der Waals radius of oxygen (see Figure 1). This $r_{V,max}$ perpendicular value for the nitro group is 2.59 Å. The half-thickness of the nitro group is equivalent to a value of $r_{V,min}$ perpendicular. While no value of the half-thickness is available, it should be approximately the same as the half-thickness of the benzene ring for which a value of 1.77 Å has been reported. If the nitro group is to be coplanar with the benzene ring to which it is attached, the $r_{V,max}$ value is the required van der Waals radius. The maximization of resonance interaction supplies a driving force for coplanarity of nitro group and benzene ring.

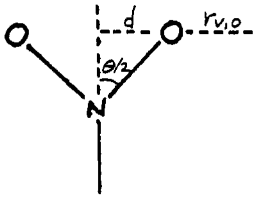

Figure 1.

For comparison purposes, the available data for the *meta*- and *para*-substituted compounds corresponding to the *ortho*-substituted sets studied were correlated with eq 2; the sets studied are those given in Table I.

Results

The results of the best correlations with eq 1 and 2 are given in Table II. Correlations with eq 3 are reported in Table III.[3]

***ortho*-Substituted Sets.** The correlation of the rates of acid hydrolysis of 2-substituted methyl benzoates (set O1) with eq 1 gave poor but significant results. None of the coefficients was significant according to the t tests. Very good results were obtained for correlation with eq 2 (set O1B). Only β gave a significant t test.

The rates of hydrogen chloride catalyzed esterification of methanol by 2-substituted benzoic acids (sets O2 to O5) gave excellent correlations with eq 1. The values of ψ in sets O2 and O4 were not significant according to the t tests. Exclusion of the value for X = NO_2 (sets O2A, O3A, O5A) gave very good to excellent correlations with no meaningful change in α, β, ψ, and h. The values of ψ were not significant in all three sets. Correlation with eq 2 gave excellent results (sets O2B-O5B). Throughout all of these sets the t tests show β to be the most important coefficient. That exclusion of the values X = NO_2 from sets O2, O3, and O5 did not cause meaningful changes in the coefficients provides some support for the choice of the van der Waals parameter for the nitro group.

The rates of hydrogen chloride catalyzed esterification of cyclohexanol by 2-substituted benzoic acids gave excellent correlations with eq 1 (sets O6–O9). Values

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[1] M. Charton, *J. Am. Chem. Soc.*, **91**, 615 (1969).

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

[3] Tables of the data used in the correlations and of the complete results of the correlations have been deposited as Document No. NAPS 00156 with the ASIS National Auxiliary Publication Service, % CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $1.00 for microfilm or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

[4] M. Charton, *J. Org. Chem.*, in press.

Table I. Sets Studied in Correlations

Set	Reaction	Ref	Solvent	Catalyst	Temp, °C	n^f in $10^n k_2$
1	$XC_6H_4CO_2Me + H_3O^+$	*a*	$MeOH-H_2O^f$		100.8	3
2	$XC_6H_4CO_2H + MeOH$	*b*	MeOH	HCl	25	4
3		*b*			40	4
4		*b*			49.9–50	4
5		*b*			60	4
6	+ c-$C_6H_{11}OH$	*c*	c-$C_6H_{11}OH$		55	5
7		*c*			65	5
8		*c*			75	5
9		*c*			85	5
10	+ MeOH	*d*	MeOH	TsOH	50	4
11		*d*			60	4
12		*d*			70	4
13	+ EtOH	*e*	EtOH	HCl	15	0

[a] N. B. Chapman, J. Shorter, and J. H. P. Utley, *J. Chem. Soc.*, 1291 (1963). [b] R. J. Hartman and A. B. Gassmann, *J. Am. Chem. Soc.*, **62**, 1559 (1940); R. J. Hartman and A. B. Gassmann, *ibid.*, **59**, 2107 (1937). [c] R. J. Hartman, H. M. Hoogsteen, and J. A. Moede, *ibid.*, **66**, 1714 (1944). [d] N. B. Chapman, M. G. Rodgers, and J. Shorter, *J. Chem. Soc., B*, 157 (1968). [e] J. J. Sudborough and M. K. Turner, *ibid.*, **101**, 237 (1912). [f] 80%v/v.

Table II. Results of Correlations with Eq 1 and 2

Set	α	β	ψ	h	R	F	r_{12}	r_{13}	r_{23}
O1	−0.0863	−2.63	0.106	−0.259	0.979	15.30	0.687	0.0224	0.730
O1B	−0.0250	−2.45		−0.0543	0.979	34.35	0.687		
O2	−0.973	−3.60	0.486	−1.49	0.997	193.8	0.257	0.523	0.901
O2B	−0.720	−2.94		−0.523	0.994	191.4	0.257		
O3	−1.08	−3.94	0.835	−1.64	0.995	141.9	0.257	0.523	0.901
O3B	−0.647	−2.81		0.00565	0.985	83.98	0.257		
O4	−0.941	−3.68	0.722	−1.11	0.994	83.18	0.191	0.695	0.886
O4B	−0.766	−2.96		0.276	0.989	86.34	0.191		
O5	−0.890	−3.70	0.896	−1.13	0.994	88.13	0.250	0.522	0.901
O5B	−0.413	−2.48		0.627	0.979	47.07	0.250		
O6	−0.344	−2.46	0.409	−1.12	0.993	95.35	0.257	0.523	0.901
O6B	−0.132	−1.90		−0.317	0.987	96.18	0.257		
O7	−0.384	−2.56	0.479	−0.879	0.993	88.04	0.257	0.523	0.901
O7B	−0.135	−1.91		0.0614	0.985	79.41	0.257		
O8	−0.396	−2.51	0.486	−0.549	0.993	91.85	0.257	0.523	0.901
O8B	−0.143	−1.85		0.403	0.984	77.42	0.257		
O9	−0.447	−2.65	0.555	−0.371	0.991	76.00	0.257	0.523	0.901
O9B	−0.158	−1.90		0.717	0.981	63.13	0.257		
O10B	−0.511	−2.29		0.343	0.991	28.59	0.729		
O11	0.0349	−0.149	−0.318	1.18	0.944	8.126	0.711	0.011	0.684
O11B	−0.126	−1.99		0.556	0.936	14.19	0.703		
O12	−0.0567	−1.85	−0.224	1.25	0.749	0.854	0.792	0.653	0.082
O12B	−0.199	−2.31		0.806	0.748	1.906	0.792		
O13	−0.0514	−1.92	−0.459	−0.608	0.987	48.89	0.026	0.593	0.757
O13C	−0.356	−2.57		−1.49	0.983	87.21	0.050		

Set	s_{est}	s_α	s_β	s_ψ	s_h	n	CL
O1	0.108	0.965	2.77	1.61	3.12	6	90.0
O1B	0.0885	0.205	0.402		0.0712	6	99.0
O2	0.0777	0.193	0.376	0.258	0.511	8	99.9
O2B	0.0955	0.170	0.169		0.0926	8	99.9
O3	0.0867	0.215	0.420	0.288	0.570	8	99.9
O3B	0.137	0.244	0.242		0.133	8	99.9
O4	0.813	0.204	0.477	0.438	0.844	7	99.5
O4B	0.0972	0.207	0.226		0.0957	7	99.9
O5	0.0948	0.241	0.466	0.319	0.633	7	99.5
O5B	0.156	0.282	0.278		0.152	7	99.5
O6	0.0674	0.167	0.326	0.223	0.443	8	99.9
O6B	0.0817	0.146	0.145		0.0792	8	99.9
O7	0.0707	0.175	0.342	0.234	0.465	8	99.9
O7B	0.0904	0.161	0.160		0.0876	8	99.9
O8	0.0671	0.167	0.325	0.223	0.442	8	99.9
O8B	0.0889	0.159	0.157		0.0861	8	99.9
O9	0.0761	0.189	0.368	0.252	0.500	8	99.9
O9B	0.101	0.181	0.179		0.0981	8	99.9
O10B	0.0565	0.179	0.333		0.0656	4	<90.0
O11	0.116	1.02	2.95	1.72	3.33	7	90.0
O11B	0.106	0.226	0.479		0.0796	7	97.5
O12	0.144	1.60	5.33	2.45	4.85	6	<90.0
O12B	0.118	0.326	1.43		0.180	6	<90.0
O13	0.103	0.392	0.765	0.525	0.995	8	99.5
O13C	0.0942	0.123	0.198		0.0540	9	99.9

Table II (*Continued*)

Set	t_α	*CL*	t_β	*CL*	t_ψ	*CL*	t_h	*CL*
O1	0.009	<20.0	0.949	50.0	0.066	<20.0	0.083	<20.0
O1B	0.122	<20.0	6.095	90.0			0.763	20.0
O2	5.041	99.0	9.574	99.9	1.884	80.0	2.916	95.0
O2B	4.235	99.0	17.40	99.9			5.756	99.0
O3	5.023	99.0	9.381	99.9	2.899	95.0	2.877	95.0
O3B	2.652	95.0	11.61	99.9			0.042	<20.0
O4	4.613	98.0	7.715	99.0	1.648	80.0	1.315	50.0
O4B	3.700	95.0	13.10	99.9			2.884	95.0
O5	3.693	95.0	7.940	99.0	2.809	90.0	1.785	80.0
O5B	1.465	50.0	8.921	99.9			4.125	98.0
O6	2.060	80.0	7.546	99.0	1.834	80.0	2.528	90.0
O6B	0.904	50.0	13.10	99.9			4.022	98.0
O7	2.194	90.0	7.485	99.0	2.047	80.0	1.890	80.0
O7B	0.839	50.0	11.94	99.9			0.701	20.0
O8	2.371	90.0	7.723	99.0	2.179	90.0	1.242	50.0
O8B	0.899	50.0	11.78	99.9			4.681	99.0
O9	2.366	90.0	7.201	99.0	2.202	90.0	0.742	50.0
O9B	0.873	50.0	10.61	99.9			7.309	99.9
O10B	2.855	50.0	7.877	90.0			5.229	80.0
O11	0.034	<20.0	0.505	20.0	0.185	<20.0	0.354	20.0
O11B	0.558	20.0	8.805	99.9			6.984	99.0
O12	0.045	<20.0	0.347	20.0	0.091	<20.0	0.258	<20.0
O12B	0.610	20.0	1.615	50.0			5.478	99.0
O13	0.013	<20.0	2.509	90.0	0.874	50.0	0.611	20.0
O13C	2.894	95.0	12.98	99.9			27.59	99.9

Set	α	β	*h*	*R*	*F*	*r*	s_{est}	s_α	s_β
M1	−0.107	−0.0807	0.986	0.545	0.211	0.207	0.103	0.170	0.412
M2	−0.564	−0.306	0.287	0.991	160.0	0.011	0.0240	0.0354	0.0379
M3	−0.576	−0.259	0.790	0.985	99.61	0.001	0.0300	0.0443	0.0473
M4	−0.609	−0.276	1.13	0.983	86.26	0.001	0.0342	0.0503	0.0539
M5	−0.602	−0.282	1.41	0.985	97.37	0.001	0.0319	0.0471	0.0504
M6	0.328	0.0834	0.250	0.813	5.854	0.001	0.0668	0.0986	0.105
M7	0.236	0.0319	0.656	0.751	3.887	0.011	0.0579	0.0854	0.0913
M8	0.138	0.0891	1.03	0.616	1.838	0.001	0.0571	0.0843	0.0902
M9	0.198	0.0423	1.33	0.847	7.637	0.001	0.0350	0.0516	0.0552
M11	−0.576	−0.212	1.44	0.993	37.99	0.207	0.0384	0.0634	0.154
P2	−0.509	0.240	0.301	0.957	27.23	0.016	0.0511	0.0757	0.0821
P3	−0.496	0.273	0.804	0.949	22.76	0.016	0.0560	0.0830	0.0900
P4	−0.519	0.323	1.14	0.950	23.36	0.016	0.0595	0.0882	0.0956
P5	−0.526	0.299	1.42	0.950	18.43	0.026	0.0657	0.0993	0.106
P6	0.630	0.939	0.245	0.958	16.85	0.633	0.0621	0.153	0.163
P7	0.729	0.971	0.631	0.958	16.74	0.633	0.0655	0.162	0.171
P8	0.652	1.01	0.981	0.952	14.45	0.633	0.0720	0.178	0.188
P9	0.491	0.859	1.30	0.964	19.95	0.633	0.0520	0.128	0.136

Set	s_h	*n*	*CL*	t_α	*CL*	t_β	*CL*	t_h	*CL*
M1	0.0779	4	90.0	0.629	20.0	0.196	20.0	12.66	90.0
M2	0.0167	9	99.9	15.93	99.9	8.073	99.9	17.19	99.9
M3	0.0209	9	99.9	13.00	99.9	5.476	99.0	37.80	99.9
M4	0.0238	9	99.9	12.11	99.9	5.121	99.0	47.48	99.9
M5	0.0222	9	99.9	12.78	99.9	5.595	99.0	63.51	99.9
M6	0.0465	9	95.0	3.326	98.0	0.794	50.0	5.376	99.9
M7	0.0403	9	90.0	2.763	95.0	0.349	20.0	16.28	99.9
M8	0.0398	9	90.0	1.637	80.0	0.988	50.0	25.87	99.9
M9	0.0244	9	97.5	3.837	99.0	0.766	50.0	54.51	99.9
M11	0.0291	4	90.0	8.139	90.0	1.377	50.0	49.48	98.0
P2	0.0363	8	99.5	6.724	99.0	2.923	95.0	8.292	99.9
P3	0.0398	8	99.5	5.976	99.0	3.033	95.0	20.20	99.9
P4	0.0423	8	99.0	5.884	99.0	3.378	98.0	26.95	99.9
P5	0.0468	7	99.0	5.297	99.0	2.821	95.0	30.34	99.9
P6	0.0467	6	97.5	4.118	95.0	5.761	98.0	5.246	98.0
P7	0.0493	6	97.5	4.500	95.0	5.678	98.0	12.80	99.0
P8	0.0541	6	95.0	3.663	95.0	5.372	98.0	28.13	99.9
P9	0.0391	6	97.5	3.863	95.0	6.316	99.0	33.25	99.9

of ψ were not significant for sets O6 and O7; α was not significant for set O5. Exclusion of the value for X = NO_2 gave only good to excellent correlations with no meaningful change in coefficients (sets O6A to O9A). Values of ψ and α were not significant in sets O6A–O9A. Correlations with eq 2 gave excellent results (sets O6B–O9B). Again, α values were not significant. Exclusion of the points for X = NO_2 gave very good to excellent correlations (sets O6C–O9C) with α values not significant. Once more, the t tests show β to be the most important coefficient.

The rates of *p*-toluenesulfonic acid catalyzed esterification of methanol by 2-substituted benzoic acids did not give good results on correlation with eq 1. The

Table III. Results of Correlations with Eq 3

Set	β	h	r	t	s	s_β	n	CL
O1D	−2.42	−0.0545	0.979	9.546	0.0768	0.253	6	99.9
O2D	−3.13	−0.849	0.970	9.800	0.186	0.319	8	99.9
O3D	−2.97	−0.279	0.965	8.955	0.194	0.332	8	99.9
O4D	−2.80	0.0746	0.949	6.714	0.183	0.417	7	99.0
O5D	−2.58	0.451	0.968	8.649	0.174	0.298	7	99.9
O6D	−1.88	−0.337	0.981	12.35	0.0911	0.152	8	99.9
O7D	−1.95	0.00204	0.982	12.90	0.0881	0.151	8	99.9
O8D	−1.89	0.340	0.982	12.61	0.0875	0.150	8	99.9
O9D	−1.94	0.648	0.978	11.43	0.0991	0.170	8	99.9
O10D	−1.59	0.346	0.918	3.723	0.121	0.487	4	90.0
O11D	−1.80	0.566	0.936	5.946	0.0952	0.303	7	99.0
O12D	−1.62	0.873	0.711	2.021	0.108	0.801	6	80.0
O13D	−2.55	−1.58	0.959	8.973	0.135	0.284	9	99.9

results for set O11 were poor; for set O12 they were not significant. Correlation with eq 2 gave good results for set O11B, and not significant results for sets O10B and O12B. It must be noted however that there are only four points in set O10B. The value for X = Me in set O12B seems much too large. Even in these sets the t tests suggest that β is the most important coefficient.

The rates of hydrogen chloride catalyzed esterification of ethanol by 2-substituted benzoic acids were correlated with eq 1 with excellent results (set O13). The values of α and ψ were not significant. Exclusion of the value for X = NO_2 gave a good correlation (set O13A). The value for X = Ac was not included in sets O13 and O13A as no van der Waals parameter is available for this group. It was included in the correlation with eq 2 (set O13B) giving results which were not significant. On excluding it (set O13 C) an excellent correlation resulted. The t tests again show β to be the most significant of the coefficients. Although r_{23} suggested that σ_R and the van der Waals parameter are related in sets O2 through O9, they are not related in sets O1, O11, and O13, all of which gave significant correlations with eq 1. We conclude that steric effects are not important in these reactions. As the t tests indicated throughout the sets studied the major importance of β, correlations with eq 3 were carried out (sets O1D through 13D). Of the O13 sets studied, nine gave excellent results, two very good results, one poor results, and one gave results which were not significant. We may conclude that, in general, *the entirety of the ortho-substituent effect upon acid-catalyzed esterification or ester hydrolysis may be represented by the resonance effect.*

***meta*-Substituted Sets.** Significant results were not obtained for the correlation of rate constants for the acid hydrolysis of 3-substituted methyl benzoates with eq 2 (set M1). Rate constants for the hydrogen chloride catalyzed esterification of methanol by 3-substituted benzoic acids gave excellent correlations with eq 2 (sets M2–M5). Rate constants for the hydrogen chloride catalyzed esterification of cyclohexanol by 3-substituted benzoic acids gave good (set M9), fair (set M6), poor (set M7), and not significant (set M8) correlations. The results obtained for the rate constants for *p*-toluenesulfonic acid catalyzed esterification of methanol by 3-substituted benzoic acids were not significant, due perhaps to the small size of the set.

***para*-Substituted Sets.** Very good (sets P3 and P4) to excellent (sets P2 and P3) correlations of rate constants for the hydrogen chloride catalyzed esterification of methanol by 4-substituted benzoic acids were obtained. The signs of α and β differ. This indicates that if the results are meaningful, the observed electrical effect must be the result of a summation of electrical effects for two or more processes, at least two of which have opposite signs.

Rate constants for the hydrogen chloride catalyzed esterification of cyclohexanol by 4-substituted benzoic acids gave fair (set P8) to good (sets P6, P7, and P9) correlations with eq 2.

Discussion

Nature of the *ortho*-Substituent Effect. We believe that our results clearly show the unimportance of steric effects as a component of the *ortho*-substituent effect upon the acid-catalyzed esterification and hydrolysis reactions. The success of the correlations with eq 3 shows that the resonance effect alone is sufficient to account for the behavior observed in esterification by *ortho*-substituted benzoic acids and acid hydrolysis of *ortho*-substituted benzoates. From the arguments presented in the first paper of this series,[4] we conclude that the steric effects must either be constant, negligible, or nonexistent. The conclusion of the second paper in this series, that the E°_S parameters do not represent steric effects but rather constitute largely a measure of σ_R, is supported by our results here. These results make necessary a reexamination of the σ_o* constants proposed by Taft[2] as a measure of the *ortho* effect.

The *ortho*-substituent effect upon basic hydrolysis of 2-substituted benzoates is very much different from that upon the acid hydrolysis or acid-catalyzed esterification reactions. Although it is also free of steric effects, it is largely or wholly localized (field) in character.[5] In describing the *ortho*-electrical effect upon the acid-catalyzed esterification let us assume that it consists of two components: the electrical effect upon the equilibrium involving the protonation of the acid

$$ArCO_2H + HA \xrightleftharpoons{K_e} ArCO_2H_2^+ + A^-$$

and that upon the rate of the reaction of the protonated acid with an alcohol

$$ROH + ArCO_2H_2^+ \xrightleftharpoons{k_r} ArC(OH)_2OHR^+$$

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(5) M. Charton, *J. Am. Chem. Soc.*, **91**, 624 (1969).

Table IV. Correlation of pK_{BH^+} for Substituted Benzoic Acids

Set	α	β	h	R	F	r	s_{est}	s_α	s_β
21	−0.141	−0.519	−7.16	0.194	0.215	0.095	0.672	0.757	0.806
21A	−2.22	−3.61	−7.59	0.932	19.87	0.466	0.275	0.468	0.614
22	−0.872	−0.171	−7.33	0.967	50.57	0.058	0.0611	0.0898	0.0836
23	−1.24	−1.41	−7.16	0.967	71.38	0.152	0.119	0.136	0.156

Set	s_h	n	CL	t_α	CL	t_β	CL	t_h	CL
21	0.199	14	<20.0	0.186	20.0	0.644	50.0	23.95	99.9
21A	0.176	9	99.5	4.744	99.0	5.879	99.0	43.13	99.9
22	0.0425	10	99.9	9.711	99.9	2.045	90.0	172.5	99.9
23	0.0558	13	99.9	9.117	99.9	9.038	99.9	128.3	99.9

Then applying eq 2 we may write for K_e and k_r

$$\log K_{e,X} = \alpha_e\sigma_{I,X} + \beta_e\sigma_{R,X} + h_e \tag{4}$$

$$\log k_{r,X} = \alpha_r\sigma_{I,X} + \beta_r\sigma_{R,X} + h_r \tag{5}$$

The rate law will be

$$v = k_r C_{ArCO_2H_2^+} C_{ROH} \tag{6}$$

and

$$K_e = \frac{C_{ArCO_2H_2^+} C_{ROH}}{C_{ArCO_2H} C_{ROH_2^+}} \tag{7}$$

or

$$v = k_r K_e C_{ArCO_2H} C_{ROH_2^+} = k_{obsd} C_{ArCO_2H} C_{ROH_2^+} \tag{8}$$

Then from eq 4, 5, and 8

$$\log k_{obsd} = \log K_e + \log k_r \tag{9}$$

$$= \alpha_e\sigma_{I,X} + \beta_e\sigma_{R,X} + h_e + \alpha_r\sigma_{I,X} + \beta_r\sigma_{R,X} + h_r \tag{10}$$

$$= \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \tag{11}$$

where

$$\begin{aligned} \alpha &= \alpha_e + \alpha_r \\ \beta &= \beta_e + \beta_r \\ h &= h_e + h_r \end{aligned} \tag{12}$$

As a model system for values of α_e and β_e let us examine the correlation with eq 2 of pK_{BH^+} values for 2-substituted benzoic acids.[3] Exclusion of the values for X = OH, H, *t*-Bu, CO_2H, and NO_2 gave an excellent correlation (set 21A). The results are presented in Table IV. Using these values for α_e and β_e we estimate $\alpha_r \sim 2.5$ and $\beta_r < 1.0$ Thus the substituent effect upon the step involving nucleophilic attack on the carbonyl group is comparable for the acid esterification and hydrolysis and for the basic hydrolysis.

***meta*-Substituted Sets.** The electrical effects observed were small and different in sign. Esterification of methanol gave negative values of α and β whereas esterification of cyclohexanol gave positive values. The values of α_e and β_e for protonation of 3-substituted benzoic acids are given in Table IV. They suggest for water values of α_r and β_r of 0.3 and −0.1. Thus unlike the *ortho* case the acidic and basic hydrolyses in water seem to have greatly different dependences on substitutent effects, as α and β for the basic hydrolyis in water are 1.6 and 0.5, respectively (estimated from the ρ value[6]). As the α and β values obtained for methanol were used to estimate α_r and β_r, the latter can be only crude approximations.

***para*-Substituted Sets.** Esterification of ethanol gave negative and positive β values. Values of α and β for the esterification of cyclohexanol were positive. Values of α_e and β_e for the model system are again reported in Table IV. The values of α_r and β_r obtained from α and β for methanol are 0.7 and 1.7, respectively. They are in much closer agreement with the values for basic hydrolysis of 1.6 and 1.6. Again, as the α and β values obtained for methanol were used in estimating α_r and β_r, these estimates must be considered extremely crude.

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(6) E. Tommila, A. Norro, R. Muren, S. Menenheimo, and E. Vuorinen, *Suomen Kemistilehti, B*, **32**, 115 (1959).