

CHEMOMETRIC ANALYSIS OF SUBSTITUENT EFFECTS. VIII. ALTERNATIVE INTERPRETATION OF SUBSTITUENT EFFECTS (AISE)

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Received April 21, 1995

Accepted May 29, 1995

Alternative interpretation of substituent effects (AISE) starts from the presumption that a substituent only possesses a single property described by a single substituent constant. This property is transmitted to the reaction centre by three different ways depending on the interaction type in the triad reaction centre – basic skeleton – substituent. For interpretation it is substantial whether or not the substituent has π electrons at the atom adjacent to the basic skeleton. If it has none, the substituent belongs to class I and operates only by its basic effect described by the mentioned single substituent constant. Substituents of class II possess a free electron pair at the atom adjacent to the basic skeleton, and those of class III have a multiple bond between the first and the second atoms which is polarized in the direction from the basic skeleton. Substituent effects in class I are described by a substituent constant identical with σ_I constant. Substituents in classes II and III show additional effects proportional to the same constant. Hence, a separate treatment of substituent effects in the individual classes provides three straight lines intersecting in a common point. Mathematically, the description of substituent effects in this approach is expressed by a family of lines with a single explaining variable. The point of intersection, which is referred to as the iso-effect point, is not identical with the classic standard substituent – hydrogen – but is near to CN substituent. The approach given has the advantage of adopting a single substituent constant whose scale can be adjusted relatively precisely. Its drawback (like in the case of the correlation equations derived from the principle of separation of substituent effects) lies in a more extensive set of substituents needed for a correlation. The AISE principle has been applied to 318 series of experimental data describing effects of 32 substituents in a large variety of chemical models (aliphatic, alicyclic, aromatic, heteroaromatic, with or without direct conjugation between reaction centre and substituent) in both chemical reactions and equilibria. A comparison with two other correlation relations with two and three substituent constants for interpretation of substituent effects based on the principle of separation of the individual substituent effects showed that the closeness of AISE based correlations is comparable with that of the correlation equations currently used. It was somewhat less successful in the models with direct conjugation between reaction centre and substituent but the AISE principle can be used even in these cases.

Since the first formulation by Hammett, the quantitative approaches to description of substituent effects have undergone a certain development also including the basic principles. A detailed description of all peripeteias of this development can be found in

literature¹⁻⁸, therefore this paper is restricted to discussion of principles used in quantitative description of substituent effects.

Hammett's approach^{1,5,7,9} can be denoted as formal in the context given. The substituent constants σ_m and σ_p include both the nature of substituent and its position at the benzene nucleus. This approach has the advantage of a single reaction constant whose determination can be achieved with few suitably chosen *meta* and *para* substituents. This is particularly advantageous in the cases where substituent effects are used as a tool for studying the changes at the reaction centre as it is the case, e.g., in mechanistic studies. A drawback of this approach lies in the fact that substituent constants must be formulated and parametrized for other basic skeletons, which generally is very impractical. As the substituent constants also include information about the basic skeleton, this approach does not enable to evaluate the effect proper (often very specific) of the substituent. The limited possibilities of the approach became even more evident when it was applied to processes involving direct conjugation between reaction centre and substituent, such as dissociations of phenols^{1,10}, solvolyses of cumyl chlorides¹¹, and other similar ones. The problem was not solved by introduction of further constants (σ_p^- , σ_p^+) either: on the contrary, it was made more complicated. The existence of processes with properties lying somewhere between those of the basic limit types only confirmed the failure of a formal description used as a general principle of quantitative interpretation of substituent effects. In this respect, the equation by Yukawa and Tsuno^{12,13} represents the peak attainable by this formal approach.

The second principle of quantitative description of substituent effects is based on a separate description of elementary substituent effects defined in a certain way^{2-9,14-23}. This approach is clearly more general than the formal approach since in the ideal case the substituent constant does not include at all the properties of the basic skeleton. The substantial problems connected with this approach lie in the definition of fundamental substituent effects and their separation in the parametrization based on experiment. Our previous paper²⁴ dealt with the inductive effect and showed that even this unambiguously fundamental effect can be interpreted in various ways. It also showed that substituent constants σ_I of different provenance include a variable extent of another effect usually denoted as mesomeric. This effect makes itself felt in chemical models with n and π electrons and is usually quantified as the substituent constant σ_R with the help of the said models. Of course, if there is no general agreement in interpretation of inductive effect, the notion of mesomeric effect, which is formally derived from the inductive effect, is still less clear. Additional introduction of substituent constants such as σ_R^0 , σ_R^- , σ_R^+ (ref.¹⁶) is a sort of repetition of the mistakes in formal approach, even though it leads to improvement in correlation fit. In our opinion, the similarity model has its limits which cannot be crossed if the requirement of generality is to be met. The principle of separate description of substituent effects was used by a number of authors. Let us mention here only some of the fairly original suggestions. Obviously the oldest one

is that by Swain and Lupton¹⁵ whose correlation equation contains two terms, F and R , describing the field effect and the mesomeric effect. Their parametrization was gradually improved¹⁸ and the resulting correlations for various substituent constants and processes can be denoted as very good. Another approach was presented by Taft and Topsom⁶. The authors suggest to express the substituent effects by means of four quantities denoted as electronegativity χ , field F , resonance R , and polarizability P , described quantitatively by the substituent constants σ_χ , σ_F , σ_R , and σ_α . These substituent constants show little interdependence for a quite high number of substituents, and the correlations adopting them for various processes are very close. It is, of course, hard to say up to which extent this is a result of the number of parameters or of their quality. A somewhat different idea (which, however, also starts from the principle of separation of substituent effects) forms the basis of the approach by Charton⁷ denoted as LDR by the author. Three substituent constants σ_l , σ_d , and σ_e describe a localized effect of substituent (which in fact is identical with σ_I), a delocalized (resonance) effect of substituent which is not affected by the reaction centre, and an additional effect of influence of reaction centre upon the substituent. Applications of LDR principle to substituent effects in various processes can be denoted as very good. Also noteworthy is the modification of the linear additive relations in the σ_R parameter, which makes these relations formally nonlinear^{25–27}. In general it can be stated that the principle of separate description of substituent effects is general and successful in the interpretations. Its drawback is that its definitions (the physico-chemical meaning) of substituent constants describing the individual effects are not unequivocal, which is connected with insufficient separation of basic effects and, partially, with the statistical requirement of larger number of substituents in correlations.

In previous papers of this series^{24,28–30} we suggested and verified on some chemical models a model of substituent effects based on an approach qualitatively different from those described above. This alternative interpretation of substituent effects (AISE) starts from the idea of substituent having a single property only which is described – in terms of quantitative description of substituent effects – by a single substituent constant. Of course, this property is transferred to the reaction centre by three different ways depending on the interaction type in the triad reaction centre – basic skeleton – substituent. As it can be seen for the interpretation it is substantial whether the substituent has any π electrons at the atom adjacent to the basic skeleton. If it has none, it belongs to class I and operates only by its basic effect described by the above-mentioned single substituent constant σ^i . Substituents of class II have a free electron pair at the atom adjacent to the basic skeleton, and substituents of class III have a multiple bond between the first and the second atoms which is polarized in the direction from the basic skeleton. As already shown the substituents of classes II and III exhibit additional effects which, however, are proportional to the substituent constant σ^i again. Thus, the separate description of effect of the substituents classified to the individual

classes will provide three straight lines intersecting in one point. The description of substituent effects in our approach is mathematically expressed by a family of lines with a single explaining variable σ^i . The point of intersection is referred to as the iso-effect point and is not identical with the classic standard substituent – hydrogen – but is near to CN substituent. The principle given has the advantage of adopting only a single substituent constant (apparently identical with σ_I) whose scale can be adjusted relatively precisely. On the other hand, it has a disadvantage (like the correlation equations derived from the principle of separation of substituent effects) in requiring a rather large number of substituents for the correlation.

The described alternative approach to interpretation of substituent effects was successfully adopted to adjust the scale for description of inductive effect, to quantitatively interpret the *ortho* effect and effects of disubstitution. The aim of the present paper is to verify the applicability of AISE on an extensive set of data taken from literature involving, inter alia, processes connected with direct conjugation between the reaction centre and substituent, and moreover to compare the possibilities of this approach with some correlation equations in current use.

CALCULATIONS

For verification of AISE, 318 series of experimental data describing substituent effects in a large variety of chemical models have been taken from literature (Table I). For the present purpose, only chemical equilibrium and rate constants have been selected. The aim was to select – for the screening – the most representative sample involving rigid aliphatic, aromatic, and heteroaromatic systems with various types of interactions between the reaction centre and substituent. The calculation involves only the series with at least 6 substituents from among 32 substituents preselected (Table II), and with a suitable combination of substituent constants. The AISE principle is expressed mathematically by an equation of family of three lines in the form (I)

$$\log k = \log k_0 + \rho_I \mathbf{1}_I(\sigma^i - \sigma_0^i) + \rho_X \mathbf{1}_X(\sigma^i - \sigma_0^i) + \rho_{XY} \mathbf{1}_{XY}(\sigma^i - \sigma_0^i) , \quad (I)$$

where $\log k$ is logarithm of rate or equilibrium constant, $\log k_0$ is the same quantity in the point of intersection of the straight lines, ρ_I , ρ_X , and ρ_{XY} are the reaction constants in relation to the substituents of classes I, II, and III, $\mathbf{1}_I$, $\mathbf{1}_X$, and $\mathbf{1}_{XY}$ are the multiplying constants assuming the value of 1 or 0 if the substituent involves the given interaction type or not, respectively, σ^i is the single substituent constant identical with σ_I constant, and σ_0^i is the corresponding quantity at the point of intersection of the straight lines with the universal value of 0.555. In spite of apparent complexity of Eq. (I), the creation of substituent constants is very simple and consists in multiplying the difference of the single substituent constant of the given substituent and the universal constant by

TABLE I

Selected sets of experimental data (at 25 °C if not otherwise stated) for testing of AISE principle, *n* number of substituted derivatives in the set

No.	Processes and chemical models	<i>n</i>	Ref.
1. Acidobasic equilibria and reaction of aliphatic and alicyclic carboxylic acids			
1	Reaction of substituted acetic acids with diphenyldiazomethane, methanol, 30 °C	13	4
2	Reaction of substituted acetic acids with diphenyldiazomethane, ethanol, 30 °C	13	4
3	Reaction of substituted acetic acids with diphenyldiazomethane, <i>tert</i> -butyl alcohol, 30 °C	13	4
4	Reaction of substituted acetic acids with diphenyldiazomethane, dimethyl sulfoxide, 30 °C	13	4
5	Dissociation of 3-substituted acrylic acids, water	7	31
6	Esterification of 3-substituted acrylic acids by diazomethane, ethanol, 30 °C	7	31
7	Cyclohexane-4-carboxylic acids, water, 24.9 °C	7	4
8	Cyclohexane-4-carboxylic acids, 50% methanol, 24.9 °C	6	4
9	Cyclohexane-4-carboxylic acids, 50% ethanol, 24.9 °C	6	4
10	3-Substituted bicyclo[1.1.1]pentane-1-carboxylic acids, 50% ethanol	7	32
11	3-Substituted bicyclo[2.2.2]octane-1-carboxylic acids, 50% ethanol	7	33
12	3-Substituted bicyclo[2.2.2]octane-1-carboxylic acids, 80% MCS	7	33
13	4-Substituted bicyclo[2.2.2]octane-1-carboxylic acids, gas	7	34
14	4-Substituted bicyclo[2.2.2]octane-1-carboxylic acids, 50% ethanol	9	35
15	4-Substituted bicyclo[2.2.2]octane-1-carboxylic acids, 50% ethanol	12	36
16	3-Substituted adamantane-1-carboxylic acids, 50% ethanol	9	4
17	6-Substituted spiro[3.3]heptane-2-carboxylic acids, ethanol	7	4
2. Acidobasic equilibria and reaction of arylaliphatic carboxylic acids			
18	Dissociation of 3-substituted phenylacetic acids, 10% ethanol	9	37
19	Dissociation of 3-substituted phenylacetic acids, 50% ethanol	11	37
20	Dissociation of 3-substituted phenylacetic acids, 75% ethanol	11	37
21	Dissociation of 4-substituted phenylacetic acids, 10% ethanol	12	37
22	Dissociation of 4-substituted phenylacetic acids, 50% ethanol	14	37
23	Dissociation of 4-substituted phenylacetic acids, 75% ethanol	16	37
24	Dissociation of 3-substituted cinnamic acids, 50% ethanol	7	38
25	Dissociation of 4-substituted cinnamic acids, 50% ethanol	8	38
26	Protonation of 3-substituted cinnamic acids, water, H ₂ SO ₄	7	38
27	Protonation of 4-substituted cinnamic acids, water, H ₂ SO ₄	7	38
3a. Acidobasic equilibria of 3-substituted benzoic acids and its derivatives			
28	Gas, 600 K	9	39
29	Water	17	40
30	Water	8	41

TABLE I
(Continued)

No.	Processes and chemical models	<i>n</i>	Ref.
31	Water	9	42
32	Water, tetrabutylammonium bromide	10	43
33	Methanol	18	40
34	Methanol	8	44
35	10% Ethanol	10	45
36	10% Ethanol	16	46
37	10% Ethanol	19	47
38	50% Ethanol	10	45
39	50% Ethanol	20	46
40	50% Ethanol	12	48
41	50% Ethanol	21	47
42	75% Ethanol	10	45
43	75% Ethanol	21	47
44	85% Ethanol	21	47
45	Ethanol	17	40
46	Ethanol	8	44
47	1-Propanol	8	44
48	1-Butanol	8	44
49	22% 2-Methyl-2-propanol	20	47
50	32% 2-Methyl-2-propanol	21	47
51	1,2-Ethanediol	8	44
52	80% 2-Methoxyethanol	12	48
53	40% Dioxane	6	49
54	41.5% Dioxane	8	50
55	60% Dioxane	6	49
56	71.5% Dioxane	8	50
57	83% Dioxane	8	50
58	Dioxane–water $\epsilon = 55$	8	44
59	Dioxane–water $\epsilon = 40$	8	44
60	Dioxane–water $\epsilon = 15$	8	44
61	10% Acetone	8	41
62	25% Acetone	8	41
63	Acetone	16	40
64	Acetonitrile	17	40
65	Dimethylformamide	18	40
66	Tetramethylene sulfone	16	40
67	Dimethyl sulfoxide	11	51
68	Nitromethane	6	52

TABLE I
(Continued)

No.	Processes and chemical models	<i>n</i>	Ref.
69	Protonation of, H ₂ SO ₄	9	53
70	Protonation of methyl benzoates, gas, 343 K	9	54
3b. Acidobasic equilibria of 4-substituted benzoic acids and its derivatives			
71	Gas, 600 K	8	39
72	Water	17	40
73	Water	8	41
74	Water	7	55
75	Water	8	42
76	Water, tetrabutylammonium bromide	10	43
77	Methanol	18	40
78	Methanol	6	44
79	10% Ethanol	12	46
80	10% Ethanol	12	47
81	50% Ethanol	20	46
82	50% Ethanol	12	48
83	50% Ethanol	17	47
84	75% Ethanol	17	47
85	85% Ethanol	11	47
86	Ethanol	17	40
87	Ethanol	6	44
88	1-Propanol	6	44
89	1-Butanol	6	44
90	22% 2-Methyl-2-propanol	9	47
91	32% 2-Methyl-2-propanol	17	47
92	1,2-Ethanediol	6	44
93	80% 2-Methoxyethanol	12	48
94	40% Dioxane	6	49
95	41.5% Dioxane	8	50
96	55% Dioxane	8	50
97	60% Dioxane	6	49
98	71.5% Dioxane	8	50
99	80% Dioxane	6	49
100	83% Dioxane	8	50
101	Dioxane–water $\epsilon = 15$	6	44
102	25% Acetone	8	41
103	Acetone	17	40
104	Acetonitrile	16	40

TABLE I
(Continued)

No.	Processes and chemical models	<i>n</i>	Ref.
105	Dimethylformamide	20	40
106	Tetramethylene sulfone	18	40
107	Dimethyl sulfoxide	11	51
108	Nitromethane	10	52
109	Protonation of 4-substituted methyl benzoates, gas, 343 K	15	54
110	Dissociation of 4-substituted benzamides, water	7	56
111	Protonation of 4-substituted benzamides, water, H ₂ SO ₄	6	57
4. Dissociation of substituted naphthalene carboxylic acids			
112	4-Substituted 1-naphthalenecarboxylic acids, 50% ethanol	9	58
113	5-Substituted 1-naphthalenecarboxylic acids, 50% ethanol	9	58
114	6-Substituted 1-naphthalenecarboxylic acids, 50% ethanol	8	58
115	7-Substituted 1-naphthalenecarboxylic acids, 50% ethanol	7	58
116	4-Substituted 2-naphthalenecarboxylic acids, 50% ethanol	10	59
117	6-Substituted 2-naphthalenecarboxylic acids, 50% ethanol	10	59
118	7-Substituted 2-naphthalenecarboxylic acids, 50% ethanol	12	59
119	8-Substituted 2-naphthalenecarboxylic acids, 50% ethanol	11	59
5a. Dissociation of 3-substituted benzenesulfonamides			
120	25% Methanol	7	60
121	50% Methanol	7	60
122	75% Methanol	7	60
123	90% Methanol	7	60
124	Methanol	7	61
125	Ethanol	7	61
126	25% Acetone	7	60
127	Acetone	7	60
128	1,2-Dichloroethane	7	60
129	Acetonitrile	7	62
130	Pyridine	7	60
131	Tetramethylene sulfone	7	60
132	Dimethyl sulfoxide	7	62
133	25% Dimethylformamide	7	60
134	50% Dimethylformamide	7	60
135	75% Dimethylformamide	7	60
136	Dimethylformamide	7	61
5b. Dissociation of 4-substituted benzenesulfonamides			
137	25% Methanol	6	60

TABLE I
(Continued)

No.	Processes and chemical models	<i>n</i>	Ref.
138	50% Methanol	7	60
139	75% Methanol	7	60
140	Methanol	7	61
141	Ethanol	6	61
142	25% Acetone	6	60
143	Acetone	7	60
144	1,2-Dichloroethane	7	60
145	Acetonitrile	7	62
146	Pyridine	7	60
147	Tetramethylene sulfone	7	60
148	Dimethyl sulfoxide	7	62
149	25% Dimethylformamide	7	60
150	50% Dimethylformamide	7	60
151	75% Dimethylformamide	7	60
152	Dimethylformamide	7	62
5c. Reactions of 4-substituted benzenesulfonates			
153	Reaction of phenacyl 4-substituted benzenesulfonates with pyridine, acetonitrile, 35 °C	6	63
6. Solvolysis of substituted alicyclic arenesulfonates			
154	1-Substituted 2- <i>exo</i> -norbornyl <i>p</i> -toluenesulfonates, 80% ethanol, 70 °C	7	64
155	6- <i>endo</i> -Substituted 2- <i>endo</i> -norbornyl <i>p</i> -toluenesulfonates, 80% ethanol, 70 °C	8	65
156	6- <i>exo</i> -Substituted 2- <i>exo</i> -norbornyl <i>p</i> -toluenesulfonates, 80% ethanol, 70 °C	18	66
157	6- <i>exo</i> -Substituted 2- <i>endo</i> -norbornyl <i>p</i> -toluenesulfonates, 80% ethanol, 70 °C	17	66
158	7- <i>anti</i> -Substituted 2- <i>exo</i> -norbornyl <i>p</i> -toluenesulfonates, 80% ethanol, 70 °C	6	67
159	7- <i>anti</i> -Substituted 2- <i>endo</i> -norbornyl <i>p</i> -toluenesulfonates, 80% ethanol, 70 °C	6	67
160	7- <i>anti</i> -Substituted 2- <i>exo</i> -norbornyl <i>p</i> -toluenesulfonates, 97% TFE, 70 °C	6	68
161	7- <i>anti</i> -Substituted 2- <i>endo</i> -norbornyl <i>p</i> -toluenesulfonates, 97% TFE, 70 °C	6	68
162	2-Substituted bicyclo[2.2.2]octyl <i>p</i> -nitrobenzenesulfonates, 80% ethanol, 70 °C	6	69
163	3-Substituted bicyclo[2.2.2]octyl <i>p</i> -nitrobenzenesulfonates, 80% ethanol, 70 °C	7	69
164	4-Substituted bicyclo[2.2.2]octyl <i>p</i> -nitrobenzenesulfonates, 80% ethanol, 70 °C	7	69
165	3-Substituted nortricyclane, water, 1 M HClO ₄ , 348.2 K	6	70
166	3-Substituted 1-adamantyl <i>p</i> -toluenesulfonates, 80% ethanol, 70 °C	10	71
167	3-Substituted 1-adamantyl <i>p</i> -toluenesulfonates, 97% TFE, 70 °C	6	68
168	4°-Substituted 2°-adamantyl <i>p</i> -nitrobenzenesulfonates, 80% ethanol, 70 °C	8	72

TABLE I
(Continued)

No.	Processes and chemical models	<i>n</i>	Ref.
7a. Reactions with formation of carbocations, 3-substituted derivatives			
169	Solvolysis of benzhydryl chlorides, methanol	8	73
170	Solvolysis of benzhydryl chlorides, ethanol	8	73
171	Solvolysis of cumyl chlorides, methanol	8	74
172	Solvolysis of cumyl chlorides, ethanol	10	74
173	Solvolysis of cumyl chlorides, 90% acetone	14	74, 75
7b. Reactions with formation of carbocations, 4-substituted derivatives			
174	Solvolysis of 4-substituted 4'-(1-chloroethyl)biphenyls, 80% acetone	7	76
175	Solvolysis 1-(1-naphthylethyl) chlorides, 80% acetone, 45 °C	7	77
176	Solvolysis of benzhydryl chlorides, methanol	7	73
177	Solvolysis of benzhydryl chlorides, ethanol	8	73
178	Solvolysis of benzhydryl chlorides, 50% ethanol, 83 °C	7	78
179	Solvolysis of diphenylcarbenium tetrafluoroborates, ethanol	14	79
180	Solvolysis of cumyl chlorides, 90% acetone	11	74, 75
181	Solvolysis of trityl chlorides, 40% ethanol–60% diethyl ether	7	80
182	Addition of bromine on styrenes, methanol	7	81
183	Methoxymercuration of styrenes, methanol	10	82
184	Beckmann rearrangements of acetophenones, 95.4% H ₂ SO ₄ , 50.9 °C	6	83
185	Beckmann rearrangement of acetophenone oxime picrylethers, 1,4-dichlorobutane, 70 °C	10	84
186	Decomposition of ω-diazoacetophenones, acetic acid, 40 °C	8	85
187	Decomposition of ω-diazoacetophenones, 75% acetic acid	8	86
8a. Acidobasic equilibria of 3-substituted anilines and its derivatives			
188	Anilines, gas, 300 °C	13	87
189	Anilines, gas, 600 °C	13	87
190	Anilines, water, 20 °C	8	88
191	Anilines, water	7	89
192	Anilines, water	8	88
193	Anilines, water	13	90
194	Anilines, water	8	91
195	Anilines, water, 30 °C	8	88
196	Anilines, water, 35 °C	8	88
197	Anilines, water, 40 °C	8	88
198	Anilines, water, $\delta\Delta H^{int}$	7	92
199	<i>N,N</i> -Dimethyl anilines, 50% ethanol	13	45
200	Anilines, dimethyl sulfoxide	7	93
201	Dissociation of <i>N</i> -phenylsulfanilamide, water, 0.033 M ethanolamine	9	93

TABLE I
(Continued)

No.	Processes and chemical models	<i>n</i>	Ref.
8b. Acidobasic equilibria of 4-substituted anilines and its derivatives			
202	Anilines, water, 20 °C	8	88
203	Anilines, water	7	89
204	Anilines, water	8	88
205	Anilines, water	13	90
206	Anilines, water	8	91
207	Anilines, water, 30 °C	8	88
208	Anilines, water, 35 °C	8	88
209	Anilines, water, 40 °C	8	88
210	Anilines, $\delta\Delta H^{\text{int}}$	7	92
211	Anilines, 50% ethanol	7	78
212	Anilines, acetonitrile	7	94
213	Anilines, dimethyl sulfoxide	9	93
214	<i>N,N</i> -Dimethyl anilines, 50% ethanol	9	45
215	Dissociation of <i>N</i> -phenylsulfanilamide, water, 0.033 M ethanolamine	9	13
9a. Acidobasic equilibria and reaction of 3-substituted phenols and its derivatives			
216	Phenols, gas	9	95
217	Phenols, gas	19	96
218	Phenols, gas, 600 K	8	38
219	Phenols, water	11	97
220	Phenols, water	8	91
221	Phenols, water	14	96
222	Phenols, 0.1 M KCl, water	7	98
223	Phenols, 20% ethanol, 20 °C	8	99
224	Phenols, dimethyl sulfoxide	6	100
225	Thiophenols, 48% ethanol	8	101
226	Reaction of phenols with isopropylmethylphosphonofluoridate, water	7	98
227	Base catalyzed hydrolysis of phenyl acetates, water	8	102
228	Base catalyzed hydrolysis of phenyl diethyl phosphates, water	7	103
229	Base catalyzed hydrolysis of phenyl <i>N</i> -methyl carbamates, water, 37 °C	9	104
230	Base catalyzed hydrolysis of phenyl <i>N,N</i> -dimethyl carbamates, water	7	102
9b. Acidobasic equilibria and reactions of 4-substituted phenols and its derivatives			
231	Phenols, gas	8	95
232	Phenols, gas	19	96
233	Phenols, gas, 600 K	8	38
234	Phenols, water	9	105

TABLE I
(Continued)

No.	Processes and chemical models	<i>n</i>	Ref.
235	Phenols, water	11	97
236	Phenols, water	8	91
237	Phenols, water	15	96
238	Phenols, water	8	15
239	Phenols, 0.1 M KCl, water	9	98
240	Phenols, 50% ethanol	10	105
241	Phenols, dimethyl sulfoxide	8	100
242	Thiophenols, 48% ethanol	8	101
243	Reaction of phenols with isopropylmethylphosphonofluoridate, water	9	98
244	Base catalyzed hydrolysis of phenyl acetates, water	10	102
245	Solvolysis of ethyl phenyl acetates, 60% acetone	13	106
246	Base catalyzed hydrolysis of phenyl diethyl phosphates, water	10	103
247	Base catalyzed hydrolysis of phenyl <i>N</i> -methyl carbamates, water, 37 °C	8	104
248	Base catalyzed hydrolysis of phenyl <i>N,N</i> -dimethyl carbamates, water	8	102
10. Acidobasic equilibria and reaction of substituted quinuclidines			
249	2-Substituted quinuclidine perchlorates, water, 0.1 M KCl	7	107
250	3-Substituted quinuclidine perchlorates, water, 0.1 M KCl	8	107
251	4-Substituted quinuclidine perchlorates, water, 0.1 M KCl	9	107
252	4-Substituted quinuclidine perchlorates, water, 0.1 M KCl	25	108
253	4-Substituted quinuclidine perchlorates, water	25	109
254	4-Substituted quinuclidine perchlorates, 5% ethanol	9	110
255	4-Substituted quinuclidine perchlorates, 50% ethanol	9	110
256	Reaction of 4-substituted quinuclidines with methyl iodide, methanol	9	110
257	Reaction of 4-substituted quinuclidines with methyl iodide, methanol	20	4
11a. Acidobasic equilibria of 2-substituted pyridines			
258	Water	18	111
11b. Acidobasic equilibria of 3-substituted pyridines			
259	Gas	13	112
260	Water, 0 °C	6	113
261	Water	20	114
262	Water	9	115
263	Water	15	116
264	Water	19	111
265	Water	13	112
266	Water, 37 °C	6	113
267	Nitromethane	7	117

TABLE I
(Continued)

No.	Processes and chemical models	<i>n</i>	Ref.
11c. Acidobasic equilibria of 4-substituted pyridines			
268	Gas	14	112
269	Water	14	112
270	Water	21	114
271	Water	15	115
272	Water	13	116
273	Water	21	111
274	Nitromethane	7	117
12. Acidobasic equilibria and reactions of other substituted heterocycles			
275	2-Substituted imidazoles, water	6	118
276	5-Substituted benzimidazoles, water	8	118
277	2-Substituted pyrimidines, water	8	119
278	3-Substituted quinolines, water	9	119
279	5-Substituted quinolines, water	8	119
280	6-Substituted quinolines, water	8	119
281	7-Substituted quinolines, water	7	119
282	8-Substituted quinolines, water	8	119
283	1-Substituted 9-aminoacridines, water	6	119
284	2-Substituted 9-aminoacridines, water	10	119
285	3-Substituted 9-aminoacridines, water	6	119
286	4-Substituted 9-aminoacridines, water	8	119
287	6-Substituted purines, water	10	118
288	8-Substituted purines, water	10	118
289	Protonation of 6-substituted purines, water	9	118
290	Protonation of 8-substituted purines, water	10	118
291	Dissociation of 4-substituted thiophene-3-carboxylic acids, water	11	120
292	Dissociation of 5-(4-substituted phenyl)furan-2-carboxylic acids, 50% ethanol	7	121
293	Dissociation of 5-(4-substituted phenoxy)furan-2-carboxylic acids, ethanol–water 1 : 1	7	122
294	Dissociation of 5-(3-substituted phenyl)tetrazoles, 50% ethanol	8	123
295	Dissociation of 5-(4-substituted phenyl)tetrazoles, 50% ethanol	11	123
296	Dissociation of 4-(4-substituted phenylamino)-5,7-dinitrobenzofurazanes, dimethylformamide	8	124
297	Protonation 1-(4-substituted phenyl)-3-methylpyrazolin-5-one, 20% ethanol, 20 °C	9	125
298	Rearrangement of 4-substituted phenylhydrazones of 3-benzoyl-5-phenyl-1,2,4-oxodiazole, dioxane–water 1 : 1	7	126
13. Acidobasic equilibria and reactions of substituted derivatives of other compounds			
299	Reaction of 3-substituted benzhydrazide with bromocycane, dimethylformamid–water 1 : 1, 20 °C	9	127

TABLE I
(Continued)

No.	Processes and chemical models	<i>n</i>	Ref.
300	Reaction of 4-substituted benzhydrazide with bromocyanide, dimethylformamide–water 1 : 1, 20 °C	9	127
301	Dissociation 4'-substituted biphenyl-2-carboxylic acids, 80% 2-methoxyethanol	10	128
302	Reaction 4'-substituted biphenyl-2-carboxylic acids with diphenyldiazomethane, 2-methoxyethanol, 30 °C	10	128
303	Dissociation of 4-(substituted methyl)benzoic acids, 80% methyl cellosolve	12	4
304	Reaction of 2-(substituted methyl)benzoic acids with diphenyldiazomethane, 40% ethanol, 0.1 M NaCl	6	129
305	Reaction of 3-(substituted methyl)benzoic acids with diphenyldiazomethane, 40% ethanol, 0.1 M NaCl	6	129
306	Dissociation of <i>N'</i> -(3-substituted benzoyl)- <i>N,N,N'</i> -trimethylhydrazinium salts, water	8	130
307	Dissociation of 1-(3-substituted phenyl)-3-phenyltriazenes, 20% ethanol, 20 °C	8	131
308	Dissociation of 1-(4-substituted phenyl)-3-phenyltriazenes, 20% ethanol, 20 °C	8	131
309	Dissociation of <i>N</i> ¹ , <i>N</i> ¹ -dimethyl- <i>N</i> ² -(3-substituted phenyl)-4-methoxybenzamidines, 95.6% ethanol	7	132
310	Dissociation of <i>N</i> ¹ , <i>N</i> ¹ -dimethyl- <i>N</i> ² -(4-substituted phenyl)-4-methoxybenzamidines, 95.6% ethanol	6	132
311	Dissociation of <i>N</i> ¹ , <i>N</i> ¹ -dimethyl- <i>N</i> ² -(3-substituted phenyl)-4-nitrobenzamidines, 95.6% ethanol	7	132
312	Dissociation of <i>N</i> ¹ , <i>N</i> ¹ -dimethyl- <i>N</i> ² -(4-substituted phenyl)-4-nitrobenzamidines, 95.6% ethanol	6	132
313	Detritiation of 3-substituted benzyl cyanides by benzylamine, dimethyl sulfoxide	7	133
314	Protonation of 3-(substituted methyl)pyridines, water	18	134
315	Protonation of 4-(substituted methyl)pyridines, water	19	135
316	Protonation of 3-substituted acetophenones, gas, 343 K	9	53
317	Protonation of 4-substituted acetophenones, water, H ₂ SO ₄	10	136
318	Basicities of 4-substituted azobenzenes, 20% ethanol, H ₂ SO ₄	7	137

zero or one. Table II presents the values of the given quantities for 32 substituents selected for testing. The respective reaction constants are then evaluated by triple linear regression. If the experimental set lacks some of the substituent types selected, the corresponding term is omitted.

In order to compare the applicability of AISE, the same data were treated with two correlation equations based on the principle of separation of substituent effects. The

TABLE II

Substituent constants σ^i (ref.²⁴), σ_I , σ_R (ref.⁸) and σ_I , σ_d , σ_e (ref.⁷) used in correlations by Eqs (1), (2), and (3); value of σ_0^i constant of Eq. (1) is equal to 0.534^a

Substituent	σ^i	1_I	1_X	1_{XY}	σ_I	σ_R	σ_I	σ_d	σ_e
H	0.000	1	0	0	0.00	0.00	0.00	0.00	0.000
CH ₃	-0.040	1	0	0	-0.01	-0.11	-0.01	-0.14	-0.030
CH ₂ CH ₃	-0.048	1	0	0	-0.01	-0.10	-0.01	-0.12	-0.036
CH(CH ₃) ₂	-0.062	1	0	0	-0.01	-0.12	0.01	-0.15	-0.040
C(CH ₃) ₃	-0.084	1	0	0	-0.01	-0.13	-0.01	-0.15	-0.036
C ₆ H ₅	0.078	1	0	0	0.12	-0.11	0.12	-0.12	-0.120
CH ₂ C ₆ H ₅	-0.018	1	0	0	0.03	-0.12	0.03	-0.13	-0.057
CF ₃	0.372	1	0	0	0.40	0.08	0.40	0.13	-0.026
CN	0.525	1	0	1	0.57	0.13	0.57	0.12	-0.055
CHO	0.385	1	0	1	0.25	0.24	0.30	0.27	-0.100
COCH ₃	0.286	1	0	1	0.30	0.16	0.30	0.25	-0.095
CONH ₂	0.250 ^a	1	0	1	0.28	0.00	0.28	0.12	-0.055
COOH	0.264	1	0	1	0.30	0.14	0.30	0.17	-0.051
COOCH ₃	0.274	1	0	1	0.30	0.14	0.32	0.16	-0.070
COOC ₂ H ₅	0.265	1	0	1	0.30	0.14	0.30	0.18	-0.064
NH ₂	0.089	1	1	0	0.17	-0.48	0.17	-0.68	-0.130
NHCH ₃	0.094	1	1	0	0.17	-0.50	0.13	-0.67	-0.180
N(CH ₃) ₂	0.089	1	1	0	0.17	-0.52	0.17	-0.66	-0.240
NHCOCH ₃	0.230	1	1	0	0.28	-0.25	0.28	-0.35	-0.088
NO ₂	0.606	1	0	1	0.67	0.15	0.67	0.18	-0.077
OH	0.157	1	1	0	0.24	-0.62	0.35	-0.57	-0.044
OCH ₃	0.220	1	1	0	0.30	-0.45	0.30	-0.55	-0.064
OC ₆ H ₅	0.278	1	1	0	0.40	-0.34	0.40	-0.51	-0.083
OCOCH ₃	0.290 ^a	1	1	0	0.38	-0.23	0.38	-0.24	-0.005
SH	0.239	1	1	0	0.27	-0.19	0.27	-0.40	-0.098
SCH ₃	0.217	1	1	0	0.30	-0.20	0.30	-0.38	-0.130
SO ₂ CH ₃	0.551	1	0	1	0.59	0.12	0.59	0.13	-0.052
SO ₂ NH ₂	0.423	1	0	0	0.44	0.12	0.44	0.18 ^b	-0.059 ^b
F	0.343 ^a	1	1	0	0.54	-0.34	0.54	-0.48	0.041
Cl	0.374	1	1	0	0.47	-0.23	0.47	-0.28	-0.011
Br	0.384	1	1	0	0.47	-0.19	0.47	-0.27	-0.018
I	0.353	1	1	0	0.40	-0.16	0.40	-0.20	-0.057

^a The optimized value on the data set from Table I. ^b The value assessed from the regression on the substituent constants set.

first of them, now already classic¹⁶, is a combination of inductive and mesomeric effects expressed by Eq. (2)

$$\log k = \log k_0 + \rho_I \sigma_I + \rho_R \sigma_R, \quad (2)$$

where σ_I and σ_R are the substituent constants describing the inductive and the resonance effects, respectively, and ρ_I and ρ_R are the corresponding reaction constants; the meaning of the other symbols is the same as in Eq. (1). The adopted parametrization taken from literature is presented in Table II. The second correlation equation chosen for comparison is the three-parameter correlation equation by Charton⁷ in the form (3)

$$\log k = \log k_0 + L\sigma_I + D\sigma_d + R\sigma_e, \quad (3)$$

where σ_I describes the localized effect of substituent, σ_d describes its intrinsic delocalized effect unaffected by the reaction centre, and σ_e reflects the additional effect of substituent affected by reaction centre. The parameters used^{7,8} are given in Table II.

RESULTS AND DISCUSSION

Success of the individual correlation equations (1), (2), (3) in the form of residual standard deviations s is compared in Table III, comparison according to individual types of chemical models in the form of overall residual standard deviation s and interpreted variability V is summarized in Table IV. For comparison: when applying the Hammett equation to logarithms of dissociation constants of *meta* and *para* substituted benzoic acids in various solvents²⁸, the obtained values were $s = 0.188$ and $V = 96.9\%$. On the basis of the data for individual sets in both tables mentioned and also on the basis of summary characteristics given at the end of Table IV it can be stated that the principle of alternative interpretation of substituent effects (AISE) suggested by us is in its applications comparable to the principle of separation of substituent effects. As AISE starts from the idea of a single effect of substituent (described by a single substituent constant) transferred to the reaction centre by three possible ways, the said conclusion also represents an argument in favour of the hypothesis given about the basis of substituent effects.

A detailed analysis of results in Tables III and IV allows further conclusions. The AISE principle is comparable with the classic correlation equations particularly for chemical models without direct conjugation between the reaction centre and substituent. The best correlation is observed with the standard models of benzoic acid (Table IV, group 3) but also with pyridines (group 11) and nonclassified models (group 13). On the other hand,

TABLE III

Residual standard deviations s in regressions by Eqs (1)–(3) on data of Table I

No.	$s(2)$	$s(3)$	$s(1)$	No.	$s(2)$	$s(3)$	$s(1)$
1. Acidobasic equilibria and reactions of aliphatic and alicyclic carboxylic acids							
1	$1.96 \cdot 10^{-2}$	$2.46 \cdot 10^{-2}$	$6.97 \cdot 10^{-3}$	10	$4.97 \cdot 10^{-2}$	$4.29 \cdot 10^{-2}$	$3.75 \cdot 10^{-2}$
2	$4.14 \cdot 10^{-2}$	$3.78 \cdot 10^{-2}$	$2.54 \cdot 10^{-2}$	11	$2.61 \cdot 10^{-2}$	$2.86 \cdot 10^{-2}$	$2.01 \cdot 10^{-2}$
3	$3.19 \cdot 10^{-2}$	$4.51 \cdot 10^{-2}$	$1.46 \cdot 10^{-2}$	12	$2.52 \cdot 10^{-2}$	$1.40 \cdot 10^{-2}$	$2.09 \cdot 10^{-2}$
4	$6.02 \cdot 10^{-2}$	$1.12 \cdot 10^{-2}$	$4.07 \cdot 10^{-2}$	13	$5.68 \cdot 10^{-2}$	$4.08 \cdot 10^{-2}$	$4.39 \cdot 10^{-2}$
5	$8.72 \cdot 10^{-2}$	$7.89 \cdot 10^{-2}$	$9.45 \cdot 10^{-2}$	14	$3.90 \cdot 10^{-2}$	$3.01 \cdot 10^{-2}$	$2.49 \cdot 10^{-2}$
6	$5.16 \cdot 10^{-2}$	$6.50 \cdot 10^{-2}$	$6.51 \cdot 10^{-2}$	15	$3.96 \cdot 10^{-2}$	$2.52 \cdot 10^{-2}$	$4.33 \cdot 10^{-2}$
7	$7.43 \cdot 10^{-1}$	$7.38 \cdot 10^{-1}$	$8.27 \cdot 10^{-1}$	16	$4.50 \cdot 10^{-2}$	$3.04 \cdot 10^{-2}$	$4.19 \cdot 10^{-2}$
8	$3.48 \cdot 10^{-3}$	$6.29 \cdot 10^{-2}$	$2.61 \cdot 10^{-2}$	17	$3.93 \cdot 10^{-2}$	$4.68 \cdot 10^{-2}$	$5.53 \cdot 10^{-2}$
9	$1.01 \cdot 10^{-2}$	$5.64 \cdot 10^{-2}$	$2.55 \cdot 10^{-2}$				
2. Acidobasic equilibria and reactions of arylaliphatic carboxylic acids							
18	$4.58 \cdot 10^{-2}$	$6.80 \cdot 10^{-2}$	$5.15 \cdot 10^{-2}$	23	$5.29 \cdot 10^{-2}$	$6.85 \cdot 10^{-2}$	$8.44 \cdot 10^{-2}$
19	$2.50 \cdot 10^{-1}$	$3.64 \cdot 10^{-2}$	$1.06 \cdot 10^{-1}$	24	$9.29 \cdot 10^{-2}$	$8.92 \cdot 10^{-2}$	$8.77 \cdot 10^{-2}$
20	$5.69 \cdot 10^{-2}$	$7.29 \cdot 10^{-2}$	$5.07 \cdot 10^{-2}$	25	$1.12 \cdot 10^{-1}$	$1.68 \cdot 10^{-1}$	$1.21 \cdot 10^{-1}$
21	$1.08 \cdot 10^{-1}$	$4.13 \cdot 10^{-2}$	$1.32 \cdot 10^{-1}$	26	1.27	$7.66 \cdot 10^{-1}$	$9.61 \cdot 10^{-1}$
22	$3.49 \cdot 10^{-2}$	$6.34 \cdot 10^{-2}$	$8.37 \cdot 10^{-2}$	27	$4.81 \cdot 10^{-2}$	$4.15 \cdot 10^{-2}$	$3.73 \cdot 10^{-2}$
3. Acidobasic equilibria of substituted benzoic acids and its derivatives							
28	$5.66 \cdot 10^{-2}$	$1.63 \cdot 10^{-2}$	$3.82 \cdot 10^{-2}$	70	$6.17 \cdot 10^{-2}$	$5.69 \cdot 10^{-2}$	$8.01 \cdot 10^{-2}$
29	$7.44 \cdot 10^1$	$2.28 \cdot 10^1$	$4.89 \cdot 10^1$	71	$7.56 \cdot 10^{-2}$	$5.28 \cdot 10^{-2}$	$9.28 \cdot 10^{-2}$
30	$6.52 \cdot 10^{-2}$	$4.94 \cdot 10^{-2}$	$5.15 \cdot 10^{-2}$	72	$2.78 \cdot 10^{-2}$	$7.19 \cdot 10^{-2}$	$4.33 \cdot 10^{-2}$
31	$7.53 \cdot 10^{-2}$	$1.10 \cdot 10^{-1}$	$9.47 \cdot 10^{-2}$	73	$6.54 \cdot 10^1$	$9.42 \cdot 10^1$	$6.82 \cdot 10^1$
32	$5.44 \cdot 10^{-2}$	$1.29 \cdot 10^{-1}$	$1.97 \cdot 10^{-2}$	74	$5.58 \cdot 10^{-2}$	$7.18 \cdot 10^{-2}$	$6.41 \cdot 10^{-2}$
33	$3.64 \cdot 10^{-2}$	$3.33 \cdot 10^{-2}$	$1.84 \cdot 10^{-2}$	75	$2.20 \cdot 10^{-1}$	$1.59 \cdot 10^{-1}$	$1.73 \cdot 10^{-1}$
34	$3.63 \cdot 10^{-2}$	$3.57 \cdot 10^{-2}$	$3.31 \cdot 10^{-2}$	76	$6.01 \cdot 10^{-2}$	$1.52 \cdot 10^{-1}$	$5.67 \cdot 10^{-2}$
35	4.50	3.48	2.32	77	$5.08 \cdot 10^{-2}$	$5.92 \cdot 10^{-2}$	$8.61 \cdot 10^{-2}$
36	$7.79 \cdot 10^{-2}$	$4.40 \cdot 10^{-2}$	$5.77 \cdot 10^{-2}$	78	3.20	3.17	4.13
37	$7.66 \cdot 10^{-2}$	$7.10 \cdot 10^{-2}$	$6.99 \cdot 10^{-2}$	79	$1.04 \cdot 10^{-1}$	$8.69 \cdot 10^{-2}$	$6.03 \cdot 10^{-2}$
38	$5.53 \cdot 10^{-2}$	$7.63 \cdot 10^{-2}$	$5.45 \cdot 10^{-2}$	80	$1.48 \cdot 10^{-1}$	$1.01 \cdot 10^{-1}$	$9.22 \cdot 10^{-2}$
39	8.05	6.23	5.93	81	9.42	3.56	5.84
40	$5.47 \cdot 10^{-2}$	$6.52 \cdot 10^{-2}$	$2.01 \cdot 10^{-2}$	82	$1.09 \cdot 10^1$	5.29	5.67
41	6.88	6.40	4.75	83	$1.23 \cdot 10^1$	7.44	8.36
42	6.64	6.91	5.41	84	$1.48 \cdot 10^{-1}$	$1.73 \cdot 10^{-1}$	$1.39 \cdot 10^{-1}$
43	$1.23 \cdot 10^{-1}$	$1.84 \cdot 10^{-1}$	$1.46 \cdot 10^{-1}$	85	$4.57 \cdot 10^{-2}$	$1.63 \cdot 10^{-1}$	$4.36 \cdot 10^{-2}$
44	$6.66 \cdot 10^{-2}$	$1.49 \cdot 10^{-1}$	$3.35 \cdot 10^{-2}$	86	$5.51 \cdot 10^{-2}$	$1.62 \cdot 10^{-1}$	$5.89 \cdot 10^{-2}$
45	$6.68 \cdot 10^{-2}$	$1.45 \cdot 10^{-1}$	$3.91 \cdot 10^{-2}$	87	$5.79 \cdot 10^{-2}$	$1.62 \cdot 10^{-1}$	$5.44 \cdot 10^{-2}$
46	$7.56 \cdot 10^{-2}$	$1.30 \cdot 10^{-1}$	$6.01 \cdot 10^{-2}$	88	2.94	4.96	5.54

TABLE III
(Continued)

No.	$s(2)$	$s(3)$	$s(1)$	No.	$s(2)$	$s(3)$	$s(1)$
47	$1.18 \cdot 10^1$	$1.02 \cdot 10^1$	9.46	89	7.07	8.44	9.06
48	$1.76 \cdot 10^1$	$1.48 \cdot 10^1$	$1.55 \cdot 10^1$	90	$6.51 \cdot 10^{-2}$	$1.19 \cdot 10^{-1}$	$5.69 \cdot 10^{-2}$
49	$4.63 \cdot 10^{-2}$	$9.39 \cdot 10^{-2}$	$1.30 \cdot 10^{-2}$	91	$1.79 \cdot 10^{-1}$	$1.54 \cdot 10^{-1}$	$1.17 \cdot 10^{-1}$
50	$9.19 \cdot 10^{-2}$	$1.14 \cdot 10^{-1}$	$8.45 \cdot 10^{-2}$	92	$2.05 \cdot 10^{-1}$	$2.64 \cdot 10^{-2}$	$9.65 \cdot 10^{-2}$
51	$1.01 \cdot 10^{-1}$	$1.04 \cdot 10^{-1}$	$1.46 \cdot 10^{-1}$	93	$4.24 \cdot 10^{-2}$	$4.65 \cdot 10^{-2}$	$4.51 \cdot 10^{-2}$
52	$1.04 \cdot 10^{-1}$	$7.17 \cdot 10^{-2}$	$7.33 \cdot 10^{-2}$	94	$4.49 \cdot 10^{-2}$	$5.09 \cdot 10^{-2}$	$5.61 \cdot 10^{-2}$
53	$1.80 \cdot 10^{-1}$	$1.54 \cdot 10^{-1}$	$1.02 \cdot 10^{-1}$	95	$1.66 \cdot 10^{-1}$	$1.38 \cdot 10^{-1}$	$1.01 \cdot 10^{-1}$
54	$4.78 \cdot 10^{-2}$	$5.21 \cdot 10^{-2}$	$4.10 \cdot 10^{-2}$	96	$5.89 \cdot 10^{-2}$	$5.90 \cdot 10^{-2}$	$5.46 \cdot 10^{-2}$
55	$7.98 \cdot 10^{-2}$	$8.58 \cdot 10^{-2}$	$3.65 \cdot 10^{-2}$	97	$1.78 \cdot 10^{-1}$	$1.31 \cdot 10^{-1}$	$8.78 \cdot 10^{-2}$
56	$4.00 \cdot 10^{-2}$	$4.47 \cdot 10^{-2}$	$3.16 \cdot 10^{-2}$	98	$7.84 \cdot 10^{-2}$	$8.42 \cdot 10^{-2}$	$3.88 \cdot 10^{-2}$
57	$5.28 \cdot 10^{-2}$	$4.79 \cdot 10^{-2}$	$3.10 \cdot 10^{-2}$	99	$7.27 \cdot 10^{-2}$	$1.55 \cdot 10^{-1}$	$7.12 \cdot 10^{-2}$
58	$3.84 \cdot 10^{-2}$	$6.75 \cdot 10^{-2}$	$3.05 \cdot 10^{-2}$	100	$1.67 \cdot 10^{-1}$	$2.79 \cdot 10^{-1}$	$1.25 \cdot 10^{-1}$
59	$1.81 \cdot 10^{-2}$	$7.12 \cdot 10^{-2}$	$2.57 \cdot 10^{-2}$	101	$2.54 \cdot 10^{-1}$	$2.80 \cdot 10^{-1}$	$2.36 \cdot 10^{-1}$
60	$4.06 \cdot 10^{-2}$	$5.65 \cdot 10^{-2}$	$6.40 \cdot 10^{-3}$	102	$3.09 \cdot 10^{-1}$	$3.13 \cdot 10^{-1}$	$2.73 \cdot 10^{-1}$
61	$2.01 \cdot 10^{-1}$	$2.71 \cdot 10^{-1}$	$2.09 \cdot 10^{-1}$	103	$3.63 \cdot 10^{-1}$	$4.22 \cdot 10^{-1}$	$3.65 \cdot 10^{-1}$
62	$1.68 \cdot 10^{-1}$	$1.90 \cdot 10^{-1}$	$1.57 \cdot 10^{-1}$	104	$3.92 \cdot 10^{-1}$	$4.29 \cdot 10^{-1}$	$3.85 \cdot 10^{-1}$
63	$1.82 \cdot 10^{-1}$	$2.54 \cdot 10^{-1}$	$2.00 \cdot 10^{-1}$	105	$2.71 \cdot 10^{-1}$	$1.56 \cdot 10^{-1}$	$1.91 \cdot 10^{-1}$
64	$2.12 \cdot 10^{-1}$	$2.74 \cdot 10^{-1}$	$2.36 \cdot 10^{-1}$	106	$7.37 \cdot 10^{-1}$	$2.58 \cdot 10^{-1}$	$4.26 \cdot 10^{-1}$
65	$1.49 \cdot 10^{-1}$	$2.19 \cdot 10^{-1}$	$1.32 \cdot 10^{-1}$	107	5.46	5.04	4.72
66	$2.77 \cdot 10^{-1}$	$6.36 \cdot 10^{-2}$	$2.36 \cdot 10^{-1}$	108	$1.19 \cdot 10^{-1}$	$4.56 \cdot 10^{-2}$	$8.05 \cdot 10^{-2}$
67	$7.16 \cdot 10^{-2}$	$4.26 \cdot 10^{-2}$	$3.80 \cdot 10^{-2}$	109	$3.66 \cdot 10^{-2}$	$1.94 \cdot 10^{-2}$	$6.81 \cdot 10^{-2}$
68	2.36	1.05	1.82	110	$3.10 \cdot 10^{-2}$	$1.47 \cdot 10^{-2}$	$1.84 \cdot 10^{-2}$
69	$5.96 \cdot 10^{-1}$	$7.03 \cdot 10^{-1}$	$9.67 \cdot 10^{-1}$	111	$2.84 \cdot 10^{-2}$	$1.58 \cdot 10^{-2}$	$1.21 \cdot 10^{-2}$
4. Dissociation of substituted naphthalene carboxylic acids							
112	$1.70 \cdot 10^{-1}$	$1.63 \cdot 10^{-1}$	$6.49 \cdot 10^{-2}$	116	$7.85 \cdot 10^{-2}$	$6.86 \cdot 10^{-2}$	$8.36 \cdot 10^{-2}$
113	$6.71 \cdot 10^{-2}$	$8.69 \cdot 10^{-2}$	$4.87 \cdot 10^{-2}$	117	$5.64 \cdot 10^{-2}$	$3.63 \cdot 10^{-2}$	$3.46 \cdot 10^{-2}$
114	$3.94 \cdot 10^{-2}$	$4.71 \cdot 10^{-2}$	$3.28 \cdot 10^{-2}$	118	$5.86 \cdot 10^{-2}$	$7.73 \cdot 10^{-2}$	$3.25 \cdot 10^{-2}$
115	$6.08 \cdot 10^{-2}$	$2.58 \cdot 10^{-2}$	$6.02 \cdot 10^{-2}$	119	$8.23 \cdot 10^{-2}$	$1.07 \cdot 10^{-1}$	$1.11 \cdot 10^{-1}$
5. Dissociation of substituted benzenesulfonamides and reactions of benzenesulfonates							
120	$2.43 \cdot 10^{-2}$	$2.83 \cdot 10^{-2}$	$2.01 \cdot 10^{-2}$	137	$3.32 \cdot 10^{-2}$	$1.77 \cdot 10^{-2}$	$4.00 \cdot 10^{-2}$
121	$3.74 \cdot 10^{-2}$	$3.76 \cdot 10^{-2}$	$3.61 \cdot 10^{-2}$	138	$3.15 \cdot 10^{-2}$	$3.41 \cdot 10^{-2}$	$3.29 \cdot 10^{-2}$
122	$4.81 \cdot 10^{-2}$	$4.36 \cdot 10^{-2}$	$4.06 \cdot 10^{-2}$	139	$4.47 \cdot 10^{-2}$	$3.25 \cdot 10^{-2}$	$1.68 \cdot 10^{-2}$
123	$2.30 \cdot 10^{-2}$	$2.67 \cdot 10^{-2}$	$1.59 \cdot 10^{-2}$	140	$4.65 \cdot 10^{-2}$	$3.49 \cdot 10^{-2}$	$1.56 \cdot 10^{-2}$
124	$6.82 \cdot 10^{-2}$	$6.82 \cdot 10^{-2}$	$5.99 \cdot 10^{-2}$	141	$1.01 \cdot 10^{-1}$	$1.03 \cdot 10^{-1}$	$5.63 \cdot 10^{-2}$
125	$8.10 \cdot 10^{-2}$	$9.16 \cdot 10^{-2}$	$1.33 \cdot 10^{-1}$	142	$7.17 \cdot 10^{-2}$	$6.02 \cdot 10^{-2}$	$4.93 \cdot 10^{-2}$
126	$4.87 \cdot 10^{-2}$	$5.68 \cdot 10^{-2}$	$5.11 \cdot 10^{-2}$	143	$1.48 \cdot 10^{-1}$	$1.21 \cdot 10^{-1}$	$1.28 \cdot 10^{-1}$
127	$1.24 \cdot 10^{-1}$	$1.07 \cdot 10^{-1}$	$1.11 \cdot 10^{-1}$	144	$8.16 \cdot 10^{-2}$	$3.49 \cdot 10^{-2}$	$9.82 \cdot 10^{-2}$

TABLE III
(Continued)

No.	$s(2)$	$s(3)$	$s(1)$	No.	$s(2)$	$s(3)$	$s(1)$
128	$1.79 \cdot 10^{-1}$	$1.61 \cdot 10^{-1}$	$2.57 \cdot 10^{-1}$	145	$9.06 \cdot 10^{-2}$	$1.05 \cdot 10^{-1}$	$7.03 \cdot 10^{-2}$
129	$6.45 \cdot 10^{-2}$	$5.32 \cdot 10^{-2}$	$4.81 \cdot 10^{-2}$	146	$1.22 \cdot 10^{-1}$	$6.80 \cdot 10^{-2}$	$1.18 \cdot 10^{-1}$
130	$4.73 \cdot 10^{-2}$	$4.29 \cdot 10^{-2}$	$5.45 \cdot 10^{-2}$	147	$1.35 \cdot 10^{-1}$	$1.42 \cdot 10^{-1}$	$1.22 \cdot 10^{-1}$
131	$1.55 \cdot 10^{-1}$	$1.38 \cdot 10^{-1}$	$1.47 \cdot 10^{-1}$	148	$2.16 \cdot 10^{-1}$	$2.32 \cdot 10^{-1}$	$2.06 \cdot 10^{-1}$
132	$1.12 \cdot 10^{-1}$	$4.40 \cdot 10^{-2}$	$1.08 \cdot 10^{-1}$	149	$4.54 \cdot 10^{-2}$	$3.20 \cdot 10^{-2}$	$4.00 \cdot 10^{-2}$
133	$1.80 \cdot 10^{-2}$	$1.38 \cdot 10^{-2}$	$1.16 \cdot 10^{-2}$	150	$4.70 \cdot 10^{-2}$	$4.23 \cdot 10^{-2}$	$5.69 \cdot 10^{-2}$
134	$3.42 \cdot 10^{-2}$	$3.06 \cdot 10^{-2}$	$2.82 \cdot 10^{-2}$	151	$5.61 \cdot 10^{-2}$	$6.70 \cdot 10^{-2}$	$4.89 \cdot 10^{-2}$
135	$6.43 \cdot 10^{-2}$	$5.71 \cdot 10^{-2}$	$5.34 \cdot 10^{-2}$	152	$8.10 \cdot 10^{-2}$	$1.10 \cdot 10^{-1}$	$9.25 \cdot 10^{-2}$
136	$8.72 \cdot 10^{-2}$	$3.88 \cdot 10^{-2}$	$7.81 \cdot 10^{-2}$	153	$1.81 \cdot 10^{-1}$	$1.82 \cdot 10^{-1}$	$1.67 \cdot 10^{-1}$
6. Solvolysis of substituted alicyclic arenesulfonates							
154	$6.19 \cdot 10^{-1}$	$5.95 \cdot 10^{-1}$	$5.18 \cdot 10^{-1}$	162	$1.13 \cdot 10^{-1}$	$1.58 \cdot 10^{-1}$	$3.12 \cdot 10^{-1}$
155	$5.47 \cdot 10^{-1}$	$5.47 \cdot 10^{-1}$	$4.62 \cdot 10^{-1}$	163	$2.02 \cdot 10^{-1}$	$1.68 \cdot 10^{-1}$	$2.01 \cdot 10^{-1}$
156	$7.64 \cdot 10^{-1}$	$6.02 \cdot 10^{-1}$	$8.64 \cdot 10^{-1}$	164	$3.72 \cdot 10^{-1}$	$3.65 \cdot 10^{-1}$	$3.59 \cdot 10^{-1}$
157	$3.53 \cdot 10^{-1}$	$4.04 \cdot 10^{-1}$	$3.66 \cdot 10^{-1}$	165	$7.99 \cdot 10^{-1}$	$2.64 \cdot 10^{-1}$	$9.30 \cdot 10^{-1}$
158	$1.11 \cdot 10^{-1}$	$1.23 \cdot 10^{-1}$	$1.11 \cdot 10^{-1}$	166	$4.45 \cdot 10^{-1}$	$2.70 \cdot 10^{-1}$	$4.35 \cdot 10^{-1}$
159	$8.28 \cdot 10^{-2}$	$4.87 \cdot 10^{-2}$	$3.77 \cdot 10^{-2}$	167	$4.20 \cdot 10^{-1}$	$4.56 \cdot 10^{-1}$	$2.13 \cdot 10^{-1}$
160	$3.57 \cdot 10^{-1}$	$3.57 \cdot 10^{-1}$	$1.96 \cdot 10^{-1}$	168	$1.53 \cdot 10^{-1}$	$1.33 \cdot 10^{-1}$	$2.02 \cdot 10^{-1}$
161	$3.03 \cdot 10^{-1}$	$2.60 \cdot 10^{-1}$	$6.69 \cdot 10^{-3}$				
7. Reactions with formation of carbocations							
169	$1.61 \cdot 10^{-1}$	$1.73 \cdot 10^{-1}$	$1.91 \cdot 10^{-1}$	179	$6.53 \cdot 10^{-1}$	$4.57 \cdot 10^{-1}$	$6.27 \cdot 10^{-1}$
170	$2.70 \cdot 10^{-1}$	$2.90 \cdot 10^{-1}$	$3.03 \cdot 10^{-1}$	180	$7.57 \cdot 10^{-1}$	$5.32 \cdot 10^{-1}$	$4.11 \cdot 10^{-1}$
171	$3.20 \cdot 10^{-1}$	$3.20 \cdot 10^{-1}$	$3.59 \cdot 10^{-1}$	181	$2.87 \cdot 10^{-1}$	$1.85 \cdot 10^{-1}$	$3.27 \cdot 10^{-1}$
172	$4.16 \cdot 10^{-1}$	$3.29 \cdot 10^{-1}$	$3.91 \cdot 10^{-1}$	182	$7.46 \cdot 10^{-1}$	$3.98 \cdot 10^{-1}$	$3.18 \cdot 10^{-1}$
173	$3.84 \cdot 10^{-1}$	$3.15 \cdot 10^{-1}$	$3.61 \cdot 10^{-1}$	183	$1.82 \cdot 10^{-1}$	$1.24 \cdot 10^{-1}$	$1.81 \cdot 10^{-1}$
174	$2.19 \cdot 10^{-1}$	$7.27 \cdot 10^{-2}$	$1.89 \cdot 10^{-1}$	184	$1.43 \cdot 10^{-1}$	$1.37 \cdot 10^{-1}$	$7.93 \cdot 10^{-2}$
175	$6.63 \cdot 10^{-1}$	$2.61 \cdot 10^{-1}$	$6.11 \cdot 10^{-1}$	185	$3.41 \cdot 10^{-1}$	$2.53 \cdot 10^{-1}$	$3.99 \cdot 10^{-1}$
176	$2.67 \cdot 10^{-1}$	$2.63 \cdot 10^{-1}$	$4.01 \cdot 10^{-1}$	186	$6.55 \cdot 10^{-2}$	$7.26 \cdot 10^{-2}$	$7.64 \cdot 10^{-2}$
177	$7.28 \cdot 10^{-1}$	$3.12 \cdot 10^{-1}$	$6.23 \cdot 10^{-1}$	187	$1.16 \cdot 10^{-1}$	$1.28 \cdot 10^{-1}$	$1.17 \cdot 10^{-1}$
178	$1.13 \cdot 10^{-1}$	$7.53 \cdot 10^{-2}$	$3.42 \cdot 10^{-1}$				
8. Acidobasic equilibria of substituted anilines and its derivatives							
188	2.70	$8.70 \cdot 10^{-1}$	1.71	202	$2.78 \cdot 10^{-1}$	$8.74 \cdot 10^{-2}$	$3.72 \cdot 10^{-1}$
189	2.86	$8.47 \cdot 10^{-1}$	1.81	203	$2.50 \cdot 10^{-1}$	$1.00 \cdot 10^{-1}$	$3.78 \cdot 10^{-1}$
190	$7.15 \cdot 10^{-2}$	$1.31 \cdot 10^{-2}$	$4.89 \cdot 10^{-2}$	204	$2.78 \cdot 10^{-1}$	$8.28 \cdot 10^{-2}$	$3.70 \cdot 10^{-1}$
191	$2.34 \cdot 10^{-1}$	$2.03 \cdot 10^{-1}$	$1.61 \cdot 10^{-1}$	205	$4.08 \cdot 10^{-1}$	$6.56 \cdot 10^{-2}$	$4.11 \cdot 10^{-1}$
192	$6.42 \cdot 10^{-2}$	$1.64 \cdot 10^{-2}$	$5.22 \cdot 10^{-2}$	206	$2.76 \cdot 10^{-1}$	$7.86 \cdot 10^{-2}$	$3.69 \cdot 10^{-1}$
193	$1.03 \cdot 10^{-1}$	$8.24 \cdot 10^{-2}$	$6.50 \cdot 10^{-2}$	207	$2.74 \cdot 10^{-1}$	$8.20 \cdot 10^{-2}$	$3.66 \cdot 10^{-1}$

TABLE III
(Continued)

No.	$s(2)$	$s(3)$	$s(1)$	No.	$s(2)$	$s(3)$	$s(1)$
194	$8.10 \cdot 10^{-2}$	$3.10 \cdot 10^{-2}$	$6.58 \cdot 10^{-2}$	208	$2.68 \cdot 10^{-1}$	$8.06 \cdot 10^{-2}$	$3.57 \cdot 10^{-1}$
195	$5.76 \cdot 10^{-2}$	$1.75 \cdot 10^{-2}$	$5.79 \cdot 10^{-2}$	209	$2.61 \cdot 10^{-1}$	$7.96 \cdot 10^{-2}$	$3.50 \cdot 10^{-1}$
196	$5.82 \cdot 10^{-2}$	$1.65 \cdot 10^{-2}$	$5.42 \cdot 10^{-2}$	210	$3.74 \cdot 10^2$	$3.36 \cdot 10^2$	$5.00 \cdot 10^2$
197	$6.86 \cdot 10^{-2}$	$1.76 \cdot 10^{-2}$	$5.55 \cdot 10^{-2}$	211	$1.54 \cdot 10^{-1}$	$5.54 \cdot 10^{-2}$	$3.04 \cdot 10^{-1}$
198	$7.19 \cdot 10^1$	$2.28 \cdot 10^1$	$6.39 \cdot 10^1$	212	$9.73 \cdot 10^{-2}$	$1.50 \cdot 10^{-1}$	$2.96 \cdot 10^{-1}$
199	$6.33 \cdot 10^{-1}$	$1.97 \cdot 10^{-1}$	$7.14 \cdot 10^{-1}$	213	1.24	1.17	1.50
200	$2.51 \cdot 10^{-1}$	$2.47 \cdot 10^{-1}$	$2.52 \cdot 10^{-1}$	214	$1.92 \cdot 10^{-1}$	$3.30 \cdot 10^{-1}$	$2.17 \cdot 10^{-1}$
201	$1.06 \cdot 10^{-1}$	$1.02 \cdot 10^{-1}$	$9.53 \cdot 10^{-2}$	215	$1.85 \cdot 10^{-1}$	$3.35 \cdot 10^{-2}$	$3.17 \cdot 10^{-1}$
9. Acidobasic properties and reactions of substituted phenols and its derivatives							
216	$8.28 \cdot 10^{-1}$	$9.45 \cdot 10^{-1}$	1.03	233	2.85	1.24	3.57
217	1.39	1.13	$8.85 \cdot 10^{-1}$	234	$3.43 \cdot 10^{-1}$	$1.43 \cdot 10^{-1}$	$4.32 \cdot 10^{-1}$
218	$9.56 \cdot 10^{-1}$	1.01	$9.71 \cdot 10^{-1}$	235	$2.38 \cdot 10^{-1}$	$1.12 \cdot 10^{-1}$	$4.74 \cdot 10^{-1}$
219	$1.15 \cdot 10^{-1}$	$1.06 \cdot 10^{-1}$	$7.14 \cdot 10^{-2}$	236	$2.91 \cdot 10^{-1}$	$1.23 \cdot 10^{-1}$	$2.86 \cdot 10^{-1}$
220	$1.04 \cdot 10^{-1}$	$9.59 \cdot 10^{-2}$	$5.59 \cdot 10^{-2}$	237	$5.36 \cdot 10^{-1}$	$2.62 \cdot 10^{-1}$	$6.99 \cdot 10^{-1}$
221	$1.19 \cdot 10^{-1}$	$9.74 \cdot 10^{-2}$	$9.23 \cdot 10^{-2}$	238	$6.73 \cdot 10^{-2}$	$4.28 \cdot 10^{-2}$	$8.08 \cdot 10^{-2}$
222	$2.97 \cdot 10^{-1}$	$5.13 \cdot 10^{-2}$	$1.70 \cdot 10^{-1}$	239	$4.99 \cdot 10^{-1}$	$1.45 \cdot 10^{-1}$	$3.77 \cdot 10^{-1}$
223	$4.59 \cdot 10^{-2}$	$5.80 \cdot 10^{-2}$	$7.41 \cdot 10^{-2}$	240	$3.81 \cdot 10^{-1}$	$2.20 \cdot 10^{-1}$	$4.65 \cdot 10^{-1}$
224	$3.62 \cdot 10^{-1}$	$3.62 \cdot 10^{-1}$	$2.54 \cdot 10^{-1}$	241	$3.72 \cdot 10^{-1}$	$3.17 \cdot 10^{-1}$	$4.72 \cdot 10^{-1}$
225	$9.49 \cdot 10^{-2}$	$9.50 \cdot 10^{-2}$	$7.36 \cdot 10^{-2}$	242	$1.06 \cdot 10^{-1}$	$3.83 \cdot 10^{-2}$	$1.48 \cdot 10^{-1}$
226	$6.17 \cdot 10^{-2}$	$7.70 \cdot 10^{-2}$	$4.59 \cdot 10^{-2}$	243	$2.57 \cdot 10^{-1}$	$1.39 \cdot 10^{-1}$	$1.81 \cdot 10^{-1}$
227	$1.17 \cdot 10^{-1}$	$1.17 \cdot 10^{-1}$	$1.47 \cdot 10^{-1}$	244	$6.39 \cdot 10^{-2}$	$5.61 \cdot 10^{-2}$	$7.19 \cdot 10^{-2}$
228	$6.71 \cdot 10^{-2}$	$4.48 \cdot 10^{-2}$	$2.05 \cdot 10^{-2}$	245	$3.14 \cdot 10^{-2}$	$2.77 \cdot 10^{-2}$	$6.85 \cdot 10^{-2}$
229	$7.82 \cdot 10^{-2}$	$8.67 \cdot 10^{-2}$	$9.82 \cdot 10^{-2}$	246	$4.09 \cdot 10^{-2}$	$6.74 \cdot 10^{-2}$	$1.59 \cdot 10^{-1}$
230	$4.51 \cdot 10^{-2}$	$2.66 \cdot 10^{-2}$	$4.00 \cdot 10^{-2}$	247	$2.53 \cdot 10^{-1}$	$3.78 \cdot 10^{-2}$	$3.12 \cdot 10^{-1}$
231	3.46	1.57	4.98	248	$5.69 \cdot 10^{-2}$	$4.50 \cdot 10^{-2}$	$5.70 \cdot 10^{-2}$
232	2.07	$8.04 \cdot 10^{-1}$	2.20				
10. Acidobasic equilibria and reactions of substituted quinuclidines							
249	$2.30 \cdot 10^{-1}$	$2.30 \cdot 10^{-1}$	$2.02 \cdot 10^{-1}$	254	$8.77 \cdot 10^{-2}$	$1.05 \cdot 10^{-1}$	$1.12 \cdot 10^{-1}$
250	$2.00 \cdot 10^{-1}$	$2.99 \cdot 10^{-1}$	$2.33 \cdot 10^{-1}$	255	$1.07 \cdot 10^{-1}$	$2.38 \cdot 10^{-1}$	$2.26 \cdot 10^{-1}$
251	$1.75 \cdot 10^{-1}$	$1.49 \cdot 10^{-1}$	$1.43 \cdot 10^{-1}$	256	$4.24 \cdot 10^{-2}$	$6.53 \cdot 10^{-2}$	$4.53 \cdot 10^{-2}$
252	$1.61 \cdot 10^{-1}$	$1.40 \cdot 10^{-1}$	$1.45 \cdot 10^{-1}$	257	$3.36 \cdot 10^{-2}$	$4.34 \cdot 10^{-2}$	$4.42 \cdot 10^{-2}$
253	$1.48 \cdot 10^{-1}$	$1.41 \cdot 10^{-1}$	$1.60 \cdot 10^{-1}$				
11. Acidobasic equilibria of substituted pyridines							
258	$7.22 \cdot 10^{-1}$	$4.83 \cdot 10^{-1}$	$7.74 \cdot 10^{-1}$	267	$6.46 \cdot 10^{-1}$	$4.20 \cdot 10^{-1}$	$3.74 \cdot 10^{-1}$
259	2.62	2.36	2.65	268	5.86	5.52	4.98
260	$3.90 \cdot 10^{-1}$	$3.90 \cdot 10^{-1}$	$2.72 \cdot 10^{-1}$	269	2.19	2.05	1.78

TABLE III
(Continued)

No.	$s(2)$	$s(3)$	$s(1)$	No.	$s(2)$	$s(3)$	$s(1)$
261	$2.96 \cdot 10^{-1}$	$1.44 \cdot 10^{-1}$	$1.90 \cdot 10^{-1}$	270	$6.15 \cdot 10^{-1}$	$3.23 \cdot 10^{-1}$	$3.74 \cdot 10^{-1}$
262	$2.65 \cdot 10^{-1}$	$1.61 \cdot 10^{-1}$	$2.01 \cdot 10^{-1}$	271	$7.50 \cdot 10^{-1}$	$5.03 \cdot 10^{-1}$	$5.40 \cdot 10^{-1}$
263	$3.21 \cdot 10^{-1}$	$1.68 \cdot 10^{-1}$	$2.48 \cdot 10^{-1}$	272	1.04	$3.76 \cdot 10^{-1}$	$6.11 \cdot 10^{-1}$
264	$1.89 \cdot 10^{-1}$	$1.44 \cdot 10^{-1}$	$1.08 \cdot 10^{-1}$	273	$6.82 \cdot 10^{-1}$	$3.14 \cdot 10^{-1}$	$4.76 \cdot 10^{-1}$
265	$3.41 \cdot 10^{-1}$	$1.88 \cdot 10^{-1}$	$2.41 \cdot 10^{-1}$	274	1.18	$1.33 \cdot 10^{-1}$	$5.71 \cdot 10^{-1}$
266	$4.31 \cdot 10^{-1}$	$4.31 \cdot 10^{-1}$	$3.52 \cdot 10^{-1}$				
12. Acidobasic equilibria and reactions of other substituted heterocycles							
275	$1.88 \cdot 10^{-1}$	$2.29 \cdot 10^{-1}$	$3.33 \cdot 10^{-1}$	287	$2.63 \cdot 10^{-1}$	$1.91 \cdot 10^{-1}$	$2.40 \cdot 10^{-1}$
276	$8.16 \cdot 10^{-2}$	$6.86 \cdot 10^{-2}$	$9.31 \cdot 10^{-2}$	288	$4.21 \cdot 10^{-1}$	$3.58 \cdot 10^{-1}$	$1.72 \cdot 10^{-1}$
277	$6.73 \cdot 10^{-1}$	$4.16 \cdot 10^{-1}$	$2.91 \cdot 10^{-1}$	289	$6.86 \cdot 10^{-1}$	$6.16 \cdot 10^{-1}$	$3.60 \cdot 10^{-1}$
278	$3.19 \cdot 10^{-1}$	$3.39 \cdot 10^{-1}$	$5.10 \cdot 10^{-1}$	290	$4.17 \cdot 10^{-1}$	$1.70 \cdot 10^{-1}$	$2.37 \cdot 10^{-1}$
279	$2.84 \cdot 10^{-1}$	$2.39 \cdot 10^{-1}$	$1.93 \cdot 10^{-1}$	291	$1.30 \cdot 10^{-1}$	$1.27 \cdot 10^{-1}$	$1.62 \cdot 10^{-1}$
280	$1.16 \cdot 10^{-1}$	$7.28 \cdot 10^{-1}$	$1.36 \cdot 10^{-1}$	292	$3.45 \cdot 10^{-2}$	$2.67 \cdot 10^{-2}$	$6.53 \cdot 10^{-2}$
281	$4.40 \cdot 10^{-1}$	$1.86 \cdot 10^{-1}$	$2.38 \cdot 10^{-1}$	293	$3.55 \cdot 10^{-2}$	$5.05 \cdot 10^{-2}$	$7.98 \cdot 10^{-2}$
282	$2.50 \cdot 10^{-1}$	$1.63 \cdot 10^{-1}$	$8.71 \cdot 10^{-2}$	294	$5.58 \cdot 10^{-2}$	$5.64 \cdot 10^{-2}$	$3.43 \cdot 10^{-2}$
283	$4.20 \cdot 10^{-1}$	$3.72 \cdot 10^{-1}$	$2.94 \cdot 10^{-1}$	295	$1.57 \cdot 10^{-1}$	$1.33 \cdot 10^{-1}$	$7.95 \cdot 10^{-2}$
284	$1.88 \cdot 10^{-1}$	$1.39 \cdot 10^{-1}$	$8.60 \cdot 10^{-2}$	296	$2.03 \cdot 10^{-1}$	$1.89 \cdot 10^{-1}$	$1.35 \cdot 10^{-1}$
285	$4.14 \cdot 10^{-1}$	$3.33 \cdot 10^{-1}$	$2.60 \cdot 10^{-1}$	297	$1.69 \cdot 10^{-1}$	$1.56 \cdot 10^{-1}$	$1.55 \cdot 10^{-1}$
286	$3.73 \cdot 10^{-1}$	$3.73 \cdot 10^{-1}$	$3.64 \cdot 10^{-1}$	298	$1.34 \cdot 10^{-2}$	$2.68 \cdot 10^{-2}$	$4.28 \cdot 10^{-2}$
13. Acidobasic equilibria and reactions of substituted derivatives of other compounds							
299	$1.05 \cdot 10^{-1}$	$1.15 \cdot 10^{-1}$	$1.52 \cdot 10^{-1}$	309	$2.07 \cdot 10^{-1}$	$2.05 \cdot 10^{-1}$	$2.42 \cdot 10^{-1}$
300	$9.01 \cdot 10^{-2}$	$9.91 \cdot 10^{-2}$	$1.27 \cdot 10^{-1}$	310	$1.85 \cdot 10^{-1}$	$1.82 \cdot 10^{-1}$	$2.99 \cdot 10^{-1}$
301	$3.69 \cdot 10^{-2}$	$3.20 \cdot 10^{-2}$	$2.45 \cdot 10^{-2}$	311	$2.05 \cdot 10^{-1}$		

TABLE IV

Comparison of overall residual deviations s (with the corresponding degrees of freedom v) and of explained variability V (in %) obtained by application of Eqs (1), (2), and (3) to data of Table I depending of type of chemical model

Groups	Eq. (2)			Eq. (3)			Eq. (1)		
	s	v	V	s	v	V	s	v	V
1	0.201	73	97.74	0.256	55	97.24	0.252	46	97.76
2	0.372	44	93.32	0.334	27	96.70	0.384	29	95.31
3	0.286	664	93.84	0.295	625	93.81	0.252	623	95.52
3a	0.261	342	95.07	0.297	313	94.18	0.253	312	95.78
3b	0.330	269	92.74	0.337	235	93.38	0.286	234	95.25
4	0.320	28	95.77	0.508	15	94.31	0.461	15	95.31
5	0.186	115	98.01	0.185	102	98.26	0.197	106	97.95
6	0.381	51	93.22	0.481	27	94.26	0.521	28	93.02
7	0.334	74	94.22	0.311	47	96.82	0.366	56	94.75
7b	0.326	41	95.50	0.337	19	97.78	0.414	26	95.40
8	0.289	121	95.35	0.177	82	98.81	0.305	100	95.73
8b	0.269	41	96.94	0.229	18	99.03	0.443	27	94.53
9	0.285	171	95.02	0.212	133	97.87	0.334	148	94.11
9b	0.329	78	94.66	0.203	44	98.85	0.481	56	91.79
10	0.209	52	97.97	0.350	27	97.04	0.354	22	97.54
11	0.405	133	89.79	0.375	97	93.59	0.351	106	93.89
12	0.346	83	94.21	0.355	57	95.81	0.386	58	94.95
13	0.331	79	94.59	0.366	53	95.56	0.326	55	96.34
11–13	0.270	2 157	94.38	0.245	2 039	95.64	0.250	2 085	95.36

a certain failure can be observed with the correlations of *para* substituted derivatives where a positive charge is formed at the atom adjacent with the aromatic ring during the reaction (group 7b) and with *para* substituted anilines (group 8b) and phenols (group 9b). In group 7b, the regression coefficient at the term expressing the additional effect of substituents class II (type X) was statistically significant in 13 cases out of 14 (nonsignificant for the set No. 181). In group 8b (anilines) the opposite was true, the regression coefficient at the term expressing the additional effect of substituents of class III (type XY) being statistically significant only in 1 case out of 14 (set No. 205). Better results were obtained in group 9b (phenoxides) where 6 regression coefficients (sets Nos 232, 236, 238, 239, 243, 248) out of 18 were statistically significant in the term for substitution type XY. The results given can be interpreted in several ways. The

first possibility is that AISE is only valid within a limited range. A possible reason is another value of intersection point σ_0^i for models with direct conjugation between the reaction centre and substituent as compared with that for standard models. As, however, the optimization showed that the sensitivity of the statistical characteristics describing the validity of the model to σ_0^i value is only average (a change by one tenth of the value near the optimum value causes changes in hundredths of the total residual deviation), this obviously is not the main cause. Another reason can be the change of the substituent effect itself upon interaction with the reaction centre, which is necessarily accompanied by a change in the quantitative characteristic of substituent property. A certain indication in this sense is the worse correlations obtained with the data for gas phase (Nos 28, 71, 188, 189, 216, 217, 231, 232, 259, 268) as compared with the results obtained in solutions, which, however, represents a problem for the other correlation relations tested, too. A backward effect of the reaction centre upon the substituent obviously cannot be fully excluded⁷, however, in the cases of distinctly charged centres, and this fact could represent the limiting factor of the AISE principle, which is based on the standard properties of substituent disregarding the chemical environment. The third (though obviously not the only) reason of the less close correlations for substituted derivatives showing direct conjugation between the reaction centre and substituent can lie in low precision of experiments. A certain indication in favour of this statement is in the comparison of sets involving formation of a carbocation (7b) where due to the great distance of important substituents (NH_2 , NHCH_3 , $\text{N}(\text{CH}_3)_2$, OH , OCH_3 , OC_6H_5 , OCOCH_3 , SH , and SCH_3) from the point of intersection of the straight lines in Eq. (1) the differences in relation to the basic line are greater than usual experimental error. On the other hand, in groups 8b, 9b the important substituents (CHO , COCH_3 , COOH , COOR , NO_2 , SO_2NH_2 , and SO_2CH_3) are near the point of intersection, and the differences related to the basic line are comparable to or lower than experimental error. With phenoxides, which are somewhat more sensitive than anilines to substituent effects, the number of statistically significant regression coefficients is higher. Generally, all the factors given (and possibly also others which have not been specified here) are obviously significant to various extents, however, the extent of their influence must be verified with better sets of substituents than are those now available in literature. Hence, the results given in this paper have shown the areas in which validity of the AISE principle should be verified. The possibility of adopting a single universal substituent constant for description of substituent effects represents an interesting alternative as compared with the correlation equations involving greater numbers of parameters.

This research was supported by the Grant Agency of the Czech Republic, Grant No. 203-94-0122.

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