ELECTROSTATIC EFFECTS ON IONIZATION EQUILIBRIA: SOLVENT DEPENDENCE

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Apparent dissociation constants of 3-substituted bicyclo[2,2,2]-octane-1-carboxylic acids *I—III* and of several substituted benzoic acids were measured in four pure solvents. The results — together with numerous literature data concerning dissociation in other solvents and in the gas phase — were compared with the prediction of the electrostatic theory. The theory fails to reproduce the essential features of the solvent dependence as it predicts generally too small effects and does not differentiate between protic and aprotic solvents. The mentioned goal cannot be achieved by any more sophisticated cavity model or by any other theory as far as it characterizes the solvent only through its bulk permittivity.

The substituent effects on ionization equilibria may be expressed within the framework of classical electrostatics as a function of solvent permittivity and of geometrical factors of the solute molecule. In previous papers of this series[1-3] we have adducted new experimental evidence and discussed in general this approach, called simply the electrostatic theory. We have restricted our considerations to an isodesmic reaction

$$\mathrm{R{-}Z{-}H} + \mathrm{Z^-} \rightleftharpoons \mathrm{R{-}Z^-} + \mathrm{Z{-}H}\,,$$

where R is a dipolar substituent. For this case the pertinent equation acquires the form[4]*

$$\log\left(K/K^0\right) = \frac{e\,\mu\cos\Theta}{2{\cdot}303kTr^2\varepsilon_{\mathrm{ef}}(4\pi\varepsilon_0)}\,, \qquad (1)$$

where μ is the substituent dipole, r its distance from the ionizable proton, and Θ the angle between μ and r. The effective relative permittivity $\varepsilon_{\mathrm{ef}}$ can be estimated

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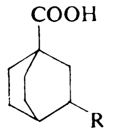
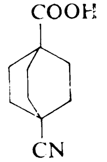
[*] In the literature[1-12] Eq. (*1*) has been written without the term $4\pi\varepsilon_0$ which is necessary when μ, e, and k are given in SI units.

from the solute geometry and from the solvent bulk permittivity (ε_{ext}) in terms of sophisticated theories, the so-called cavity models[5–10]. The reviews[11,12] reveal that a reasonable adherence to Eq. (*1*) has been considered a proof in favour of the transmission through space (field effect) and against the alternative, the transmission through bonds (σ-inductive effect). We have already pointed out[1] that this long-standing problem is ill-defined. The transmission of substituent effect must take place through space but we are faced with the question how this space can be better approximated: as a homogeneous matter with a uniform permittivity, or rather in topological terms as a system of discrete bonds.



I, R = H
II, R = Br
III, R = CN
IV, R = Cl



V

We have already critically resumed[1] the experimental possibilities how Eq. (*1*) can be verified. Most attention has been paid to syntheses of model compounds with well-defined parameters r and θ (ref.[1–3], references cited therein and further[13–15]). Another test of fundamental importance is the dependence on solvent. It is just in this point that the electrostatic theory clearly exceeds the through-bonds-transmission theory. If Eq. (*1*) were able to predict the solvent dependence at least semiquantitatively, it would be clearly superior to any through-bond description in which the solvent effect can be introduced only as an empirical proportionality factor. However, this test has been relatively little exploited[16–24]. In early studies either the effective permittivity was not calculated at all[16,18,19,21], or with some untenable assumptions[17,19,20,22]. In addition, the results obtained in mixed solvents[17,21,23,24] may be impaired by differential solvation[17]. We collected[23] dissociation constants of 4-nitrobenzoic acid, including our own measurements[23], and drew the conclusion that none of the simpler cavity models[5–8] accounts even qualitatively for the observed solvent effects. One can argue[17] that the possible mesomeric substituent effect was neglected; this applies also to previous studies using substituted benzoic acids[16–19,21]. For this reason we report in this note the dissociation constants of 3-substituted bicyclo[2,2,2]octane-1-carboxylic acids *I*–*III* in four pure solvents. Of similar compounds several 4-substituted bicyclo[2,2,2]octane-1-carboxylic acids were measured but only by the indicator method[22], besides several cyclohexanecarboxylic acids either with unsuitable substituents[20] or in mixed solvents[24]. Since our results were very similar to those with aromatic acids, we have not extended the investigation in this direction. On the other hand, we complemented earlier measurements of *ortho* derivatives[16,17] using 2-fluorobenzoic acid. The intention was to compare the results to our studies of electrostatic effects on conformational equilibria in which methyl 2-fluorobenzoate served as the best model compound[25,26]. Several other aromatic acids were included as reference compounds. These were particularly necessary for the solvent butanol, whereas comparative values in dimethyl sulfoxide[27], methanol[28], and 1,2-ethanediol[28] were available from previous measurements in our laboratory. Finally, a comparison with gas phase acidities[29,30] was carried out.

RESULTS AND DISCUSSION

The experimental dissociation constants listed in Table I are of limited reliability. While the reproducibility in repeated experiments can be estimated to ±0·03 log units, the difference against literature data[17,31–34] may attain more than one unit. For our purpose only the relative values with respect to the unsubstituted acid are of importance. Even of these, only the values measured in methanol are in satisfactory agreement with the literature[17,31] while significant deviations were observed particularly in butanol and 1,2-ethanediol, see the footnotes to Table I. Note that differences of the same order (several tenth of log unit) are observed between the literature data themselves[17,33,34]. The possible uncertainty is not decisive for further conclusions which are based more on the gross pattern than on the behaviour of a single compound in a particular solvent.

We firstly plotted the logarithms of relative dissociation constants of compound *II* against the reciprocal of solvent bulk permittivity ε_{ext}^{-1} (Fig. 1). Essentially the same pattern was obtained for compound *III* (not shown), further also for its isomer 4-cyanobicyclo[2,2,2]octane-1-carboxylic acid (*V*) using the literature data[22] (Fig. 1). The plots can be compared to the prediction of the electrostatic theory, Eq. (*1*). According to most of the cavity models[5–7,9], ε_{ef}^{-1} is a linear function of ε_{ext}^{-1}; for any such model it must be at least a single-valued function for a given solute. For instance the Kirkwood–Westheimer spherical model[5] leads to the equation:

$$\varepsilon_{ef}^{-1} = \left(1 - \frac{4x^{3/2}}{(1+x)^2}\right)\varepsilon_{int}^{-1} + \left[\frac{8x^{3/2}}{(1+x)^2} + \frac{4x^{1/2}}{1+x} - \frac{4\ln(1+x)}{x^{1/2}}\right]\varepsilon_{ext}^{-1}\,, \qquad (2)$$

where x is a simple function of r and of the radius of the spherical cavity R.

Confrontation of theory and experiment yields the same picture as obtained previously for aromatic acids[23]. We can infer that conjugation of the substituent and/or specific solvation of the benzene nucleus are of no significance, at least with respect to other imperfections of the theory. For this reason we reproduce in Fig. 2 the graph[23] for 4-nitrobenzoic acid, completed by new data[35]. Note that conjugation of the nitro group in 4-nitrobenzoic acid is in any case very weak, almost negligible[36].

TABLE I

Apparent dissociation constants of selected acids in pure solvents

Acid	pK [log (K/K^0)]			
	methanol	butanol	1,2-ethanediol	dimethyl sulfoxide
I	10·28	11·50	8·68	12·83
II	9·91 [0·37]	10·74 [0·76]	8·19 [0·49]	12·30 [0·53]
III	9·60 [0·68]	10·34 [1·16]	7·92 [0·76]	12·03 [0·80]
Benzoic	9·44	10·23	7·65	11·01
2-Fluorobenzoic	8·47 [0·97][a]	9·25 [0·98][a]	7·23 [0·42][c]	9·83 [1·18]
3-Chlorobenzoic		9·46 [0·77][b]		9·82[d] [1·19]
3-Bromobenzoic	8·81 [0·63][a]	9·37 [0·86][b]	7·43 [0·22][c]	9·91[d] [1·10][e]
3-Nitrobenzoic	8·42 [1·02][a]	8·69 [1·54][b]	6·73 [0·92][a]	9·20[d] [1·81][a]
4-Nitrobenzoic	8·41 [1·03][a]	8·41 [1·82][b]	6·59 [1·06][a]	9·07[d] [1·94][a]

[a] The relative values in satisfactory agreement with the literature[17,32]; [b] the measured substitutent effect distinctly higher than in ref.[17]; [c] the substituent effect distinctly lower than in ref.[17]; [d] previous measurements from our laboratory[27]; [e] the substituent effect lower than in ref.[32].

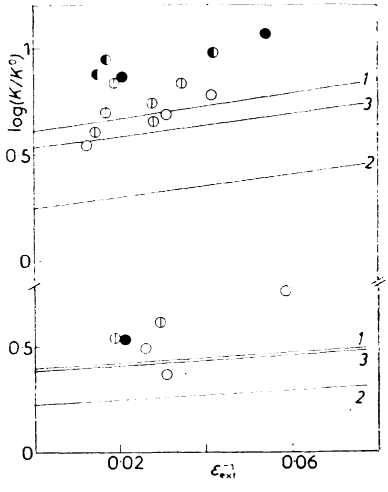


FIG. 1

Dependence of relative dissociation constants of 3-bromobicyclo[2,2,2]octane-1-carboxylic acid (at the top) and of 4-cyanobicyclo[2,2,2]octane-1-carboxylic acid[22] (at the bottom) on reciprocal of the bulk permittivity of the solvent; ○ protic solvents, ● aprotic solvents, ◐ aqueous mixtures with protic solvents, ◐ aqueous mixtures with aprotic solvents; the lines were calculated according to the following cavity models: *1* Kirkwood–Westheimer sphere[5] in Tanford modification[8], *2* Westheimer-Kirkwood ellipsoid[6,46] in Tanford modification[8], *3* Ehrenson ellipsoid[9].

The results from all the acids investigated may be summarized and discussed together:

1) There is a clear difference between pure and mixed aqueous solvents, even among aqueous mixtures with various second component. These differences cannot be accounted for by any theory which characterizes the solvent only by the permittivity value. Qualitatively they can be discussed in terms of the competition of solvation and substituent effects, breaking the water structure by the added solvent, and preferential solvation of ions by water molecules[23]. It follows that small concentration of a foreign solvent in water has a strong effect which is levelled at higher concentrations. An extrapolation[21] to $\varepsilon_{ext} \rightarrow \infty$ from 2–3 points in mixed solvent is physically meaningless and the intercept cannot be interpreted as the non-electrostatical effect.

2) Even in pure solvents only, the substituents effect is usually stronger in aprotic than in protic solvents of the same permittivity; the ratio may attain 2 : 1. This phenomenon may be also understood as a manifestation of competition of solvation and substituent effects.

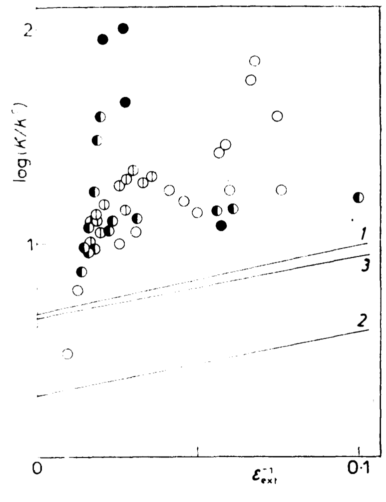


FIG. 2

Dependence of the relative dissociation constant of 4-nitrobenzoic acid[35] on reciprocal of the solvent bulk permittivity; symbols as in Fig. 1

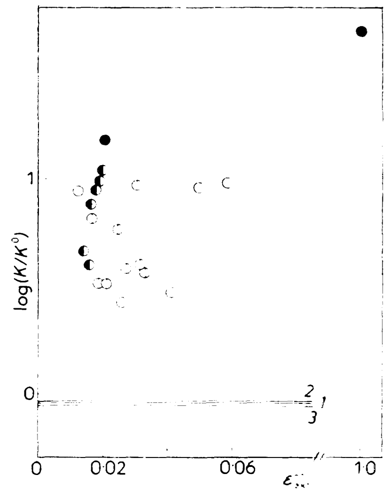


FIG. 3

Dependence of the relative dissociation constants of 2-fluorobenzoic acid (ref.[35] and this work) on reciprocal of the solvent bulk permittivity; symbols as in Fig. 1.

3) If we confine ourselves to pure protic solvents, *i.e.* essentially to water and alcohols, there is a rough dependence on ε_{ext}^{-1} which is, however, not well reproduced by the theory. Most of the cavity models yield still a high effective permittivity, hence they predict too small substituent effects. What is still more important, the dependence on solvent is badly underestimated. One can say in other words that when ε_{ef} is finally reduced to an acceptable value by a sophisticated model, this is achieved at the cost of virtual independence of solvent at all.

The above conclusions are also in accord with the results obtained with 2-fluorobenzoic acid (Fig. 3). Striking is the still more irregular pattern of experimental points and the constant predicted effect. One can argue that *ortho*-substituted derivatives are not suitable models due to some special proximity effects and to the irregular molecular shape which can be hardly embeded into a regular-shaped cavity. However, the conformational equilibrium of *ap* and *sp* rotamers of methyl 2-fluorobenzoate was in resonable agreement with electrostatic calculations[25] and the plot of ΔG^0 *vs* ε_{ext}^{-1} was linear[26]. The principal difference between the two applications may not consist in the imperfect cavity model since it is observed even in the mere experimental solvent dependence. Another explanation may be in terms of specific solvation effects of ions, but we suggested[26] that the most probable explanation is the substituent effect on bond energies since in conformational equilibria no bond is broken.

The latter hypothesis may be tested referring to gas phase dissociation of the acids under examination[29,30]. The relevant data are assembled in Table II. In this reaction there are no solvation phenomena and no cavity model is needed: one can simply examine the range of possible values of ε_{ef} between 1 and 2. Table II reveals, however, that even $\varepsilon_{ef} = 1$ is too high, *i.e.* all the calculated substituent

TABLE II

Comparison of calculated and experimental relative dissociation constants in the gas phase

Acid	Experiment		Calculated $\log (K/K^0)^a$	
	$\delta \Delta G^0$ kJ mol^{-1}	$\log (K/K^0)$ (298 K)	$\varepsilon_{ef} = 1$	$\varepsilon_{ef} = 2$
IV	$16{\cdot}3^b$	2·86	1·82	0·91
III	$26{\cdot}8^b$	4·69	3·28	1·64
V	$35{\cdot}1^b$	6·16	3·42	1·71
2-Fluorobenzoic	$9{\cdot}6^c$	$1{\cdot}68^d$	−0·14	−0·07
3-Chlorobenzoic	$19{\cdot}7^c$	$3{\cdot}45^d$	1·85	0·92
4-Nitrobenzoic	$49{\cdot}0^c$	$8{\cdot}58^d$	3·68	1·84

[a] See Experimental; [b] at 298 K, ref.[29]; [c] at 600 K, ref.[30]; [d] calculated assuming $\delta \Delta S = 0$.

effects are too low. With 2-fluorobenzoic acid even the sign is wrong but this result is very sensitive to the exact value of Θ which is near to 90° (see Table III for the details of calculation). For this acid also the substituent effect in the gas phase is comparable to that in solution, so that it can be pictured in Fig. 2. A somewhat better agreement for certain gas phase dissociations was achieved by several ad hoc corrections[37]: *a*) introducing the induced dipole in the ion, *b*) accounting for the dipole-dipole interaction in the neutral molecule, and *c*) shortening the distance r just to the carboxyl oxygen atoms instead to the hydrogen atom. Concerning these corrections: *a*) The substituent polarizability is of importance in aliphatic carboxylic acids[38], in aromatic acids the calculated affect is mostly negligible[37]. *b*) A dipole is in fact present even in the $COO^{(-)}$ group of the anion[13,24]. *c*) Measuring the distance r from the hydrogen atom is related to the electrostatic work necessary to shift the proton from its position to infinity; in other words, this accounts for the O—H dipole in the acid. Even with all correction terms the calculated values for the most powerful substituents were too low[37]. We suggest tentatively that this disagreement, too, may be attached to changes of bond energy with substitution but further evidence is needed to this point. Note that some gas-phase equilibria in which no ions

TABLE III

Electrostatic calculations of dissociation constants according to Eqs (*3*) and (*4*)

Acid	r (pm) θ (°)	A Eq. (*3*)	Sphere[a] f_1 f_2	Ellipsoid[b] f_1 f_2	Ellipsoid[c] f_1 f_2
II	575 54·5	1·7781	0·2232 0·7582	0·1296 0·6592	0·2170 0·7014
III	643 46·7	3·2754	0·2045 0·8038	0·1032 0·7461	0·1727 0·7788
V	760 0	3·4211	0·1784 0·8663	0·0742 0·8243	0·1554 0·8151
2-Fluorobenzoic	373 91·5	−0·1401	0·3007 0·5598	0·2417 0·3973	0·3389 0·4266
3-Chlorobenzoic	580 40·0	1·8461	0·2217 0·7618	0·1272 0·6638	0·2106 0·7151
4-Nitrobenzoic	742 0	3·6812	0·1820 0·8578	0·0788 0·8034	0·1761 0·7804

[a] Kirkwood–Westheimer[5] sphere in the Tanford modification[8]; [b] Westheimer–Kirkwood ellipsoid[6] in the Tanford[8] modification and the with correction[46]; [c] Ehrenson ellipsoid[9]; f_1, f_2 defined in Eq. (*4*).

are involved can be reasonably predicted by electrostatic calculations[39]; in this case some bonds are broken but changes in bond energy may compensate. In any case the electrostatic theory does not satisfy for gas-phase ionization equilibria and this statement does not depend on any particular cavity model. In order to reach better agreement with experiments either additional correction terms would be necessary, or at least the geometrical parameters r and Θ must acquire different values than in solution.

Summarizing the existing evidence for and against the electrostatic theory, we must state that the experimental material is rather unsystematic. Many ingenious model compounds have been synthetized but most of them were carboxylic acids and their dissociation was investigated only in mixed solvents, mainly in 50% ethanol. We have already pointed out the necessity of extending the investigation to ammonium ions and other cationic acids[2], now we can add that this should be done in pure solvents. Nevertheless, the evidence is sufficient for the following conclusions to be drawn:

The electrostatic theory is not able to reproduce the behaviour in various solvents as far as the properties of the solvent are reduced to its mere permittivity ε_{ext}. This statement follows from the fact that solvents of the same permittivity give rise to different effects on the equilibria.

Specific solvation may be responsible for these differences but cannot explain the generally too small predicted effects; this follows from the data in the gas phase. Designing new cavity models, however sophisticated they might be, or their reparametrization cannot help. In this respect the through-bonds model is perhaps not better but certainly more flexible as it includes the solvent dependence into an empirical proportionality constant, which can be then interpreted or predicted in terms of different theories[40].

If the task is restricted to describe the behaviour in a given solvent (or in several very similar solvents), suitable parametrization of the cavity model is possible. Acceptable results may be obtained[2] for the dependence on the substituent dipole μ and in some degree on the geometrical parameters r and Θ. In particular, the reversed substituent effect in certain unusual model compounds with $\Theta > 90°$ (*e.g.*[14] and further references discussed in [1]) may be predicted, at least qualitatively. Even in a single solvent, however, the parametrization is strictly valid only for a certain functional group[2] (commonly COOH), and a reasonable fit for many compounds may be obtained even on the basis of the through-bonds transmission[3]. If the through-bonds model is compared with the electrostatic theory, they appear as two opposite approximations. The former, as a topological approach, neglects the position of the substituent and fails completely *e.g.* for stereoisomers or in the case of reversed substituent effect. The latter, on the contrary, overestimates this effect as it neglects the inhomogeneity of the space (*i.e.* the enhanced electron density between atoms). With respect to the change of the functional group, the through-bonds model is again more flexible since it makes use of an empirical proportionality constant. We stress once more that the transmissions through space and through bonds should be viewed as mathematical approximations[1,2] and not as physical phenomena. Physically meaningless are also the attempts to describe them as two independently operating mechanisms[12,41,42], one of them being possibly controlled by the electronegativity of the substituent[12].The latter term, however, has beeen defined as the proximity effect[43] and its transmission through several bonds has not been proven. On the other hand, the concept of molecular lines of force[41], transmitting the substituent effect, is near to the description of inhomogeneous space used by us.

EXPERIMENTAL

The racemic 3-substituted bicyclo[2,2,2]octane-1-carboxylic acids *I*—*III* were described[2].

The potentiometric determination of dissociation constants was carried out using a Radiometer RTS 622 registering titration apparatus and a glass indication electrode Radiometer G 2040 C. As a reference electrode was used either a silver electrode together with a junction filled with 0·1 mol l^{-1} solution of $AgNO_3$ (for measurements in dimethyl sulfoxide), or a saturated calomel electrode and a junction filled with saturated solution of LiCl (for measurements in the remaining solvents). Solutions of the acids at the concentration $5 . 10^{-3}$ mol l^{-1} were titrated at 25 ± 0·1°C, with a 0·1 mol l^{-1} solution of tetrabutylammonium hydroxide in the respective solvent, the solution was stirred with a stream of nitrogen. The half-neutralization points were read off in mV and converted to the p*K* scale using the titration curve of benzoic acids (the slope was always near to the theoretical value of 58 mV/pH) and its p*K* values from the literature[17,32]. Every measurement was carried out four times and the average values are given in Table I. The standard deviation from the average was between 0·01 log units (in methanol) and 0.03 (in butanol).

The electrostatic calculations of the relative dissociation constants of acids *II*— *V* and substituded benzoic acids were realized on the basis of Eq. (*1*), introducing the difference $\mu_X - \mu_H$ for μ. Standard bond and group moments[44] were used (in 10^{-30} Cm): C_{al}—H −1·0, C_{ar}—H 0, C_{al}—Br 5·67, C_{ar}—F 4·90, C_{ar}—Cl 5·34, C≡N 12·01, NO_2 13·34. These values have been retained even in the calculations of gas-phase values, although the dipole moments measured in the gas phase would be somewhat higher. The difference is not important for the results.

The geometrical parameters r and Θ for acids *II*—*IV* were the same as described previously[2]. In the case of benzoic acids the distance r and the angle Θ were determined from the standard geometrical parameters[45]: bond lengths (in pm) C—C in the aromatic ring 140, C_{ar}—C(O) 146, C—F 133, C—Cl 170, C—N 140, N—O 124; bond angles all 120°, including the benzene ring. The ionizable proton of the carboxyl group was localized as usual[5] at the distance of 145 pm from the carboxyl carbon in the direction of the C_{ar}—C(O) bond.

As far as the solvent dependence of electrostatic effects on ionization equilibria is concerned, Eq. (*1*) may be written more conveniently as

$$\log (K/K^0) = A\varepsilon_{ef}^{-1} , \qquad (3)$$

where A includes all the physical constants, substituent dipole moment and geometrical parameters for the particular acid.

The effective relative permittivity ε_{ef} is then linearly dependent on the solvent bulk permittivity ε_{ext}:

$$\varepsilon_{ef}^{-1} = f_1 + f_2\varepsilon_{ext}^{-1} , \qquad (4)$$

where in the term f_1 the internal relative permittivity ε_{int} is involved, taken as 2 in any case.

The linear relationship between ε_{ef}^{-1} and ε_{ext}^{-1} was calculated using three different cavity models: *1*) the Kirkwood–Westheimer sphere[5] in the Tanford modification[8], *i.e.* with the proton and the substituent point dipole localized in the depth $d = 150$ pm under the cavity surface, *2*) Westheimer -Kirkwood ellipsoid[6] in the same modification[8], but corrected according to Edward[46], *3*) modified ellipsoidal model of Ehrenson[9] with the proton 160 pm and the point dipole 260 pm under the cavity surface. The geometrical parameters r, Θ and calculated terms A, f_1 and f_2 are given in Table III.

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