

## Limitation of the Hepler Theory of the Hammett Equation

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Deeper analysis of the assumptions of the Hepler theory leads to the conclusion that for most cases the entropy contributions to the substituent effect cannot be neglected. Hence a limitation of the Hepler theory is apparent.

HEPLER<sup>1,2</sup> developed a theory of the Hammett equation leading to expression (1) where  $\Delta G$ ,  $\Delta H_{\text{int}}$ , and  $\Delta S$  are standard free enthalpy, internal enthalpy and entropy change, respectively,  $\delta$  is the Leffler-Grunwald

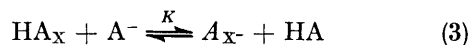
$$\delta\Delta G = \delta\Delta H_{\text{int}} + (\beta_{\text{iso}} - T) \delta\Delta S \quad (1)$$

operator<sup>3</sup> and  $\beta_{\text{iso}}$  and  $T$  the isoequilibrium temperature and temperature, respectively, both in  $K$ .

One of the consequences of the theory is that for values of  $T$  not too far from  $\beta_{\text{iso}}$  the substituent effect may be interpreted as due chiefly to intramolecular changes of energy, since we have for this case expression (2):

$$\delta\Delta G \simeq \delta\Delta H_{\text{int}} \quad (2)$$

The theory holds for acid-base equilibria written as in expression (3): where HA and HA<sub>X</sub> stand for un-



substituted and substituted acids, respectively.† For equilibrium (3) one can write

$$\log K = -\delta\Delta G/2.303 RT \quad (4)$$

Writing for this case the Hammett equation one obtains expression (5):

$$\rho\sigma = \log K = \frac{-\delta\Delta G}{2.303 RT} \simeq \frac{-\delta\Delta H_{\text{int}}}{2.303 RT} \left[ \frac{\text{const}}{2.303 RT} \right] \left[ \frac{-\delta\Delta H_{\text{int}}}{\text{const}} \right] \quad (5)$$

The first right-hand side term can readily be identified with the reaction constant  $\rho$  (temperature dependent) and the second term with substituent constant  $\sigma$  (structure dependent).

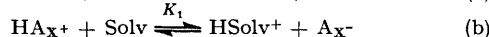
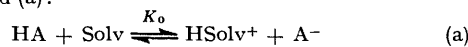
The Hepler theory has recently been both criticized<sup>4</sup> and also extended to provide a more detailed analysis of equation (5).<sup>5-7</sup> The aim of this paper is to show that entropy contributions to the overall substituent effect should also be taken into account.

According to the theory<sup>1,2</sup> the enthalpy and entropy contributions can be taken as the sum of internal and external parts:

$$\delta\Delta H = \delta\Delta H_{\text{int}} + \delta\Delta H_{\text{ext}} \quad (6a)$$

$$\text{and} \quad \delta\Delta S = \delta\Delta S_{\text{int}} + \delta\Delta S_{\text{ext}} \quad (6b)$$

† Equation (3) can be obtained by formal subtraction of reaction (b) and (a):



Then  $K = K_1/K_0$  and hence (3). For details see refs. 2.

External contributions to the entropy and enthalpy are associated with solute-solvent interactions and internal contributions arise from differences in entropy and enthalpy within the acid molecule and its anion. According to Pitzer<sup>8</sup> the internal entropy of dissociation of weak acids as in equation (3) is very near to zero. Hence we make the assumption shown in (7).

$$\delta\Delta S \simeq \delta\Delta S_{\text{ext}} \quad (7)$$

Then for ion-solvent interaction one can write equation (1) as in (8) where  $\beta_{\text{ext}}$  is the external isoequilibrium

$$\delta\Delta H_{\text{ext}} = \beta_{\text{ext}} \delta\Delta S_{\text{ext}} \simeq \beta_{\text{ext}} \delta\Delta S \quad (8)$$

temperature. The theory assumes that such proportionality does exist. Here, whilst we do not reject this assumption we analyse the sign of  $\beta_{\text{ext}}$  and draw certain conclusions.

We start our analysis by writing the expression for the iso-equilibrium temperature as in expression (9):

$$\frac{\delta\Delta H}{\delta\Delta S} = \frac{\delta\Delta H_{\text{ext}} + \delta\Delta H_{\text{int}}}{\delta\Delta S_{\text{ext}} + \delta\Delta S_{\text{int}}} = \beta_{\text{iso}} \quad (9)$$

Bearing in mind that  $\delta\Delta S_{\text{int}} \simeq 0$ , we obtain

$$\frac{\delta\Delta H_{\text{ext}} + \delta\Delta H_{\text{int}}}{\delta\Delta S_{\text{ext}}} = \beta_{\text{iso}} \quad (10)$$

Replacing in equation (10)  $\delta\Delta S_{\text{ext}}$  by  $\delta\Delta H_{\text{ext}}/\beta_{\text{ext}}$  from equation (8) one obtains after rearrangement equation (11).

$$\frac{\delta\Delta H_{\text{int}}}{\delta\Delta H_{\text{ext}}} = \frac{\beta_{\text{iso}}}{\beta_{\text{ext}}} - 1 \quad (11)$$

Discussion of this equation provides some valuable information about mutual relations between internal and external contributions to the enthalpy. These quantities are, as a rule, not experimentally accessible. However it is clear that their ratio can be analysed if the sign of  $\beta_{\text{ext}}$  is known. Usually it is expected that the stronger the solute-solvent interactions, *i.e.* the more negative  $\delta\Delta H_{\text{ext}}$ , the higher the ordering of the solvent molecules around the solute, and hence the greater the decrease of  $\delta\Delta S_{\text{ext}}$ . Thus, since  $\delta\Delta H_{\text{ext}} < 0$  and  $\delta\Delta S < 0$  their ratio has to be positive, *i.e.*  $\beta_{\text{ext}} > 0$ . Bearing this result in mind we can discuss equation (11) in more detail.

(i) For  $\beta_{\text{iso}} < \beta_{\text{ext}}$  one has

$$\frac{\delta\Delta H_{\text{int}}}{\delta\Delta H_{\text{ext}}} < 0$$

However the exact value for  $\beta_{\text{ext}}$  is, in general, not known.<sup>9</sup> Thus, since  $\beta_{\text{ext}} > 0$  one can conclude that at least for  $\beta_{\text{iso}} < 0$ ,  $\delta\Delta H_{\text{int}}$  and  $\delta\Delta H_{\text{ext}}$  have to be opposite in sign. This agrees with the well known fact that for  $\beta_{\text{iso}} = 0$  the internal and external contributions to enthalpy cancel out since  $\delta\Delta H = 0$  holds for isoenthalpic reactions.<sup>10</sup> For this case substituent effects are due to entropy changes.

(ii) For  $\beta_{\text{iso}} \simeq \beta_{\text{ext}}$  one obtains  $\delta\Delta H_{\text{int}} \simeq 0$  and the substituent effect is due to entropy or external enthalpy contributions.

(iii) For  $\beta_{\text{iso}} > \beta_{\text{ext}}$  one finds

$$\frac{\delta\Delta H_{\text{int}}}{\delta\Delta H_{\text{ext}}} > 0$$

As a consequence it is seen that both enthalpy terms have to be of the same sign. However absolute values of internal contribution can be greater than the external one only if  $\beta_{\text{iso}} > 2\beta_{\text{ext}}$  since from equation (11) it is found that because  $\beta_{\text{iso}} = 2\beta_{\text{ext}}$ ,  $\delta\Delta H_{\text{int}} = \delta\Delta H_{\text{ext}}$ . Thus, the Hepler theory holds for the case where  $\beta_{\text{iso}} \gg 2\beta_{\text{ext}}$ . Since the exact values of  $\beta_{\text{ext}}$  are unknown it is difficult to say when this case occurs. However if the customary assumption is valid, that  $\beta_{\text{ext}} \simeq T_{\text{experiment}}$ , then the higher  $\beta_{\text{iso}}$  the more significant is the internal enthalpy term and the greater the validity of the Hepler theory.

Finally one may write that for cases (i) and (ii), the internal contributions to the enthalpy are of negligible importance and the entropy contribution to the overall substituent effect has to be taken into account at least for case (i). The Hepler theory holds only for particular cases of type (iii) *i.e.* when the isoequilibrium temperature  $\beta_{\text{iso}}$  is much greater than the external isoequilibrium temperature  $\beta_{\text{ext}}$ .

Although there is no way of directly checking the above presented conclusions since most of the quantities used in derivation of the Hepler theory are not experimentally accessible, their validity is illustrated by considering the following cases.

For proton dissociation equilibria of substituted pyridinium ions Exner<sup>11</sup> estimated  $\beta_{\text{iso}} = 3\,670$  K using the experimental data of Bellobono and Monetti.<sup>12</sup> This case is similar to the isoentropic reaction series, when  $\beta_{\text{iso}} \rightarrow \infty$  and hence  $\delta\Delta S \rightarrow 0$  (for details see *e.g.* ref. 10) and, according to the analysis presented in this paper, should follow the Hepler theory. This conclusion is in accord with analysis of variance\* calculated from experimental data.<sup>12</sup> Using variances

\*  $\text{Var.}(y) = \sum_{i=1}^N (y_i + y)^2/N$  is a measure of differentiation of elements  $y_i$ .

of  $\delta\Delta H$  and  $T\delta\Delta S$  as measures of variation of  $\delta\Delta H$  and  $T\delta\Delta S$  due to the substituent effect, we are able to compare these quantities and to conclude which is more significant:  $\text{var.}(\delta\Delta H) = 16.70 \cdot 10^6 \text{ cal}^2$  and  $\text{var.}(T\delta\Delta S) = 1.24 \cdot 10^6 \text{ cal}^2$ ; thus the ratio of variances  $R = \text{var.}(\delta\Delta H)/\text{var.}(T\delta\Delta S) = 13.47$ . It means that variation in  $\delta\Delta H$  due to the substituent effect is 13.47 times greater than the variation in  $T\delta\Delta S$ , in spite of possible cancellations of  $\delta\Delta H_{\text{int}}$  and  $\delta\Delta H_{\text{ext}}$  terms. The latter effect cannot be too large in view of the high value of ratio  $R$ .

The other case is concerned with the acid-base equilibria of substituted benzoic acids. Exner<sup>11</sup> estimated  $\beta_{\text{iso}} = -40$  K, whereas Hepler<sup>13</sup> using more recent data found  $\beta_{\text{iso}} = -220$  K. In terms of our analysis this case belongs to class (i). Analysis of the variance of  $\delta\Delta H$  and  $T\delta\Delta S$  for 16 substituted benzoic acids leads to the following result:  $\text{var.}(\delta\Delta H) = 20\,785 \text{ cal}^2$  and  $\text{var.}(T\delta\Delta S) = 199\,067 \text{ cal}^2$ . The ratio  $R$  is now 0.1044 and it means that the situation is the reverse of the former example: the variation in entropy in enthalpy terms by a factor of  $1/0.1044 = 10$ . This conclusion is in line with prediction of our analysis that for (i) cases the entropy terms are of great importance.

The arguments about significance of the entropy contribution to the substituent effect were also shown when the Hammett equation with entropic and enthalpic substituent constants<sup>14,15</sup> was applied to more than 50 kinetic and equilibrium data sets.

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