ENTHALPY–ENTROPY RELATIONSHIP FOR SOME *PARA* AND *META* BENZOIC DERIVATIVES: STATISTICS AND THERMODYNAMIC THEORIES

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ABSTRACT

Statistical and thermodynamic theories regarding the requirements for the validity of the Hammett equation are compared.

The differences between the two theories can be ascribed to the fact that the same problem is considered by different points of view.

INTRODUCTION

Several authors [1–5] have hypothesized that, for a symmetrical reaction such as

$$R–PhCOOH + PhCOO^- = R–PhCOO^- + PhCOOH$$
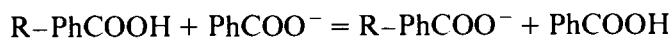
the validity of the Hammett equation requires that the differences in entropy change are proportional to the difference in enthalpy change

$$\delta\Delta H = \beta\delta\Delta S \tag{1}$$

For an equilibrium set, we can write

$$\delta\Delta G = \delta\Delta H - T/\beta\delta\Delta H \tag{2}$$

and again

$$\delta\Delta G = \delta\Delta H(1 - T/\beta) \tag{3}$$

β has the dimensions of temperature, and if $T = \beta$, all equilibria in the set have the same equilibrium constants, since $\delta\Delta G$ is zero.

The constant β is thus known as the isoequilibrium temperature, and the theory is accordingly called the linear enthalpy–entropy relationship, the isoequilibrium relationship or the compensation law.

Equation (3), obtained by hypothesizing a proportionality between $\delta\Delta H$ and $\delta\Delta S$, implies that $\delta\Delta G$ is also proportional to $\delta\Delta H$.

Although many reactions which follow the Hammett relationship have $\delta\Delta H$ values proportional to $\delta\Delta G$, this is not always the case.

Hepler carried out a thermodynamic analysis [6] in which the isoequilibrium "temperature", β_i, is a function of the temperature, and not a constant. It was also shown that the Hammett equation often provides a good approximate correlation of the equilibrium constant, even when enthalpies and entropies vary in an apparently erratic fashion and there is not a good isoequilibrium relationship.

Furthermore, contributions to $\delta\Delta H$ and $\delta\Delta S$ are considered in terms of external, or environmental, and internal factors. According to Hepler [6], environmental effects arise from solute–solvent interactions while internal effects are those intrinsic to the molecules of the acid and base.

A useful expression of the proportional relationship between $\delta\Delta H_e$ and $\delta\Delta S_e$ is

$$\delta\Delta H_e = \beta_e \delta\Delta S_e + \gamma\delta\Delta H_{in}$$

where β_e is an "environmental" parameter (different to β_i). Thus, the following equation can be written

$$\delta\Delta G = \delta\Delta H_{in}(1 + \gamma) + (\beta_e - T)\delta\Delta S$$

If $\beta_e = T$ and $\delta\Delta G = \delta\Delta H_{in}(1 + \gamma)$, then

$$\rho\sigma = \left[C(1 + \gamma)/2.303RT\right]\left[\delta\Delta H_{in}/C\right]$$

where γ is the solute–solvent interaction parameter, dependent on the solvent temperature and pressure, and the reaction type.

It is the "compensation" of $\delta\Delta H_e$ and $\delta\Delta S_e$ that accounts for the Hammett equation being approximately satisfied even when $\delta\Delta H$ and $\delta\Delta S$ vary oppositely to the exact thermodynamic requirements.

On the other hand, a correct statistical treatment [7] of thermodynamic reaction quantities within a series of related reactions requires a direct calorimetric determination of ΔH^0 and an electrochemical determination of ΔG^0.

Therefore, from a statistical point of view, only a linear regression in the coordinates ΔH^0 vs. ΔG^0 is correct, since the two variables have been obtained directly and quite independently from each other.

Thus, regressions in the coordinates ΔH^0 vs. ΔS^0 and ΔG^0 vs. ΔS^0 are misleading and yield uncorrected values for the slope and correlation coefficient; this being due to the a priori dependence of the two quantities.

This problem is treated as coordinate transformations in a plane. In the first transformation, ΔH^0 vs. ΔG^0 was changed in the ΔH^0 vs. ΔS^0 plane, while in the second, in the ΔS^0 vs. ΔG^0 plane. It is therefore possible to find the dependence of the correlation coefficients, r_{SH} and r_{GS}, on r_{GH}. These dependences illustrate that some good fits are underestimated with incorrect (ΔS^0 vs. ΔG^0 and ΔH^0 vs. ΔS^0) coordinates, and some fits are overestimated.

The false correlation coefficient r_{SH} is higher than the true r_{GH} coefficient when $r_{GH} < 1/2(S_H/S_G)$ (S_H and S_G are the standard deviations of the variables ΔH^0 and ΔG^0 from their mean values). This inequality usually holds for small r_{GH}, and always when r_{GH} is negative, and when the variance of ΔH^0 is large ($S_H/S_G > 2$). In these conditions the validity of the ΔH^0 vs. ΔS^0 plot will be overestimated. When r_{GH} is positive and the variation of ΔG^0 is larger than that of ΔH^0 (small S_H/S_G), then the ΔH^0 vs. ΔS^0 plot will be underestimated.

The ΔS^0 vs. ΔG^0 plot is generally overestimated when r_{GH} is small (always when r_{GH} is negative or when the variation of ΔG^0 is larger than that of ΔH^0 (always when $S_H/S_G < 0.50$). All these conditions are summarized by the inequality $r_{GH} < 1/2 S_G/S_H$.

Thus, the key factors for understanding when the equations ΔH^0 vs. ΔG^0, ΔH^0 vs. ΔS^0 and ΔS^0 vs. ΔG^0 give a true picture of the real relationship, are the correlation coefficient, r_{GH}, and the ratio between the standard deviations, S_H/S_G.

In the present work, some benzoic acid derivatives, have been chosen in order to check these equations in solutions in which the dielectric constant changes uniformly.

The compounds chosen display a wide range of features: the *meta*-chloro derivative presents only an inductive effect, the *meta*-hydroxy derivative an inductive effect and strong solute–solvent interactions, the *para*-methoxy derivative a strong resonance effect, and the *para*-hydroxy derivative, resonance and solute–solvent interactions. It is also well known that the two *para* derivatives fall clearly above any reasonable straight-line passing through the points of other benzoic derivatives [8] in a graph of ΔG^0 vs. ΔS^0.

EXPERIMENTAL AND PROCEDURE

The calorimetric apparatus, preparation of the DMSO–water mixtures, and the technique for obtaining the thermodynamic values for the *para* and *meta* derivatives have been previously described [9–11].

RESULTS

Table 1 shows the r_{GH}, r_{SH} and r_{GS} values as a function of the DMSO mole fraction. These data are plotted against X_{DMSO} in Fig. 1. Table 2 shows the S_H/S_G values as a function of the DMSO mole-fraction.

DISCUSSION

Figure 1 shows that r_{SH} values are clearly overestimated in DMSO-rich solutions, while in the same solutions, the r_{GS} values are underestimated. This is true even at $X_{DMSO} = 0.2$.

TABLE 1

Values of correlation coefficients as a function of the DMSO mole fraction

X_{DMSO}	r_{GH}	r_{SH}	r_{GS}
0.0	0.860	-0.560	-0.900
0.1	0.730	0.890	0.810
0.2	0.577	0.870	0.096
0.3	0.880	0.800	0.416
0.4	0.780	0.984	0.860
0.5	0.640	0.640	-0.182
0.6	0.580	0.950	0.360
0.7	0.340	0.970	0.130
0.8	0.260	0.560	-0.630

At the various mole fractions the three plots are influenced by r_{GH} and S_H/S_G in the following way.

In pure water ($r_{GH} = 0.860$) the ratio $S_H/S_G = 0.527$ shows an underestimated correlation with $\delta\Delta H$ vs. $\delta\Delta S$ ($r_{SH} = -0.560$) but a good correlation with ΔS^0 vs. ΔG^0 ($r_{GS} = -0.900$). The low value of S_H/S_G indicates that $\delta\Delta H$ values do not change appreciably from one compound to another, and the entropy term is therefore decisive.
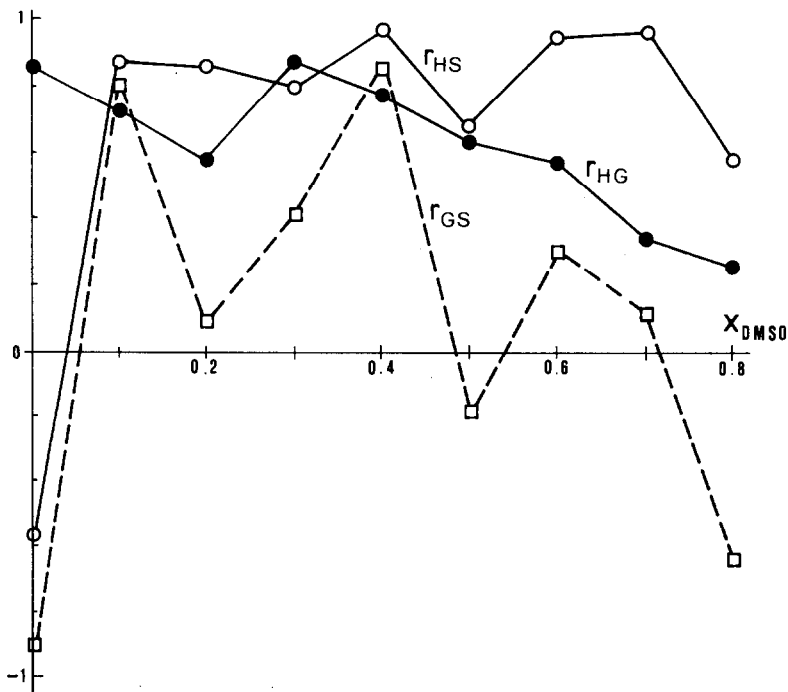

Fig. 1. Variation of the correlation coefficients as a function of the DMSO mole fraction.

TABLE 2

Values of the S_H/S_G ratio as a function of the DMSO mole fraction

X_{DMSO}	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
S_H/S_G	0.527	1.010	2.000	1.520	4.410	1.900	3.120	4.330	0.952

At $X_{DMSO} = 0.1$, $r_{GH} = 0.730$ and $S_H/S_G = 1.01$; the key factor is r_{GH}, which makes both $r_{SH} = 0.890$ and $r_{GS} = 0.810$ overestimated. A value of $r_{GH} = 0.577$ at $X_{DMSO} = 0.2$ shows that there is no correlation between the experimental quantities $\delta\Delta H^0$ and $\delta\Delta G^0$. The variation of $\delta\Delta H^0$ is larger than that of $\delta\Delta G^0$ ($S_H/S_G = 2$) so that $\delta\Delta H^0$ vs. $\delta\Delta S^0$ is overestimated ($r_{SH} = 0.870$), since this plot shows only the dependence of $\delta\Delta H^0$ on itself. The $\delta\Delta S^0$ vs. $\delta\Delta G^0$ plot is underestimated ($r_{GS} = 0.096$). Values of $r_{GH} = 0.880$ and $S_H/S_G = 1.520$ at $X_{DMSO} = 0.3$ overestimate $r_{SH} = 0.800$ and underestimate $r_{GS} = 0.416$, although not to a large extent. At $X_{DMSO} = 0.4$, $r_{GH} = 0.780$ is smaller, but $S_H/S_G = 4.410$ is much greater than 2, so that there is a large variation of $\delta\Delta H^0$ with respect to $\delta\Delta G^0$: thus, $r_{SH} = 0.984$ is clearly overestimated. For $r_{GS} = 0.860$, the overestimate is due to the small change in $\delta\Delta S^0$. At $X_{DMSO} = 0.5$ there is no correlation between the fit either in the primary independent coordinates ($r_{GH} = 0.640$, $S_H/S_G = 1.9$) or in the incorrect coordinates ($r_{SH} = 0.640$, $r_{GS} = -0.182$). At $X_{DMSO} = 0.6$, the coefficient r_{GH} is small (0.580) and S_H/S_G is large (3.120). Because of the large value of S_H/S_G, the $\delta\Delta H^0$ vs. $\delta\Delta S^0$ plot is overestimated ($r_{SH} = 0.950$) and $\delta\Delta S$ vs. $\delta\Delta G$ is underestimated ($r_{GS} = 0.36$). Again, at $X_{DMSO} = 0.7$, there is no correlation ($r_{GH} = 0.34$) between $\delta\Delta H^0$ and $\delta\Delta G^0$, while $\delta\Delta H^0$ vs. $\delta\Delta S^0$ is overestimated ($r_{SH} = 0.970$), because of the dependence of $\delta\Delta H^0$ on itself ($S_H/S_G = 4.33$), and $r_{GS} = 0.130$ is underestimated.

Finally, in the last mole fraction range ($X_{DMSO} = 0.8$; $r_{GH} = 0.260$, $S_H/S_G = 0.957$) there is no correlation for $\delta\Delta H^0$ vs. $\delta\Delta G^0$, $\delta\Delta H^0$ vs. $\delta\Delta S^0$ ($r_{SH} = 0.560$) and $\delta\Delta S^0$ vs. $\delta\Delta G^0$ ($r_{GS} = -0.630$).

In Table 3 the values of the real isoequilibrium temperatures are reported. These were calculated by means of the equation $\beta = Tb_{HG}/(b_{HG} - 1)$, where b_{HG} is the slope in the coordinate $\delta\Delta H^0$ vs. $\delta\Delta G^0$ and was calculated as $b_{HG} = (S_H/S_G)r_{GH}$.

At the 0.0, 0.1 and 0.8 DMSO mole fractions, the dissociation reaction displays so-called anticompensation, while in the remaining, it displays compensation [7].

It can be concluded that at 0.0, 0.1, 0.3, 0.4 mole fraction of DMSO, a real correlation between the experimental quantities $\delta\Delta H^0$ vs. $\delta\Delta G^0$ exists, so that the validity of the isoequilibrium relationship could be proven within the limits of a certain accuracy.

At other mole fractions no real correlation exists, but an apparent correlation may appear in one of the possible incorrect coordinate systems.

TABLE 3

Values of isoequilibrium temperature, β, as a function of the DMSO mole fraction

X_{DMSO}	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
β (K)	-247	-835.52	2234	1183	420	1653	670	936	-118

One of the reasons for this behaviour could be the large variance of $\delta\Delta H^0$ in DMSO-rich solutions, with a consequently very high value of S_H/S_G.

On the other hand, in previous works [12–14] the relationship between the isoequilibrium temperature parameter, β_i, and the "environmental" parameter, β_e, was examined.

The equations used are

$$\beta_i = \beta_e - \frac{1+\gamma}{\dfrac{\partial\gamma}{\partial T}} = T - \frac{1+\gamma}{\dfrac{\partial\gamma}{\partial T}} \tag{4}$$

$$\delta\Delta S = -\delta\Delta H_{in}\left(\frac{\partial\gamma}{\partial T}\right) \tag{5}$$

These two equations can provide β_i values, at 298.16 K for the *ortho, meta* and *para* derivatives of the chloro-, nitro- and hydroxybenzoic acids.

Equations (4) and (5) are only good for the *meta* derivatives. This confirms that requirements for an isoequilibrium relationship are more stringent than those for the free-energy relationship: the resonance effect must have small variations compared to the field effect.

It was also found [15] that the *para*-hydroxy derivative displays negative values of the substituent constant, σ, throughout the whole mole fraction range. This fact was related to the electron-releasing resonance effect which overlaps and prevails over the inductive effect.

It is also well known that the substituent with a negative σ value exhibits an "abnormal" enthalpy–entropy relationship. It has also been shown [8] how the compensation of $\delta\Delta H^0$ and $\delta\Delta S^0$ may lead to an approximate linear free-energy relationship, such as $-\delta\Delta G = 2.303RT\rho\sigma$, for the same compounds.

Therefore, in order to assess [15] the relative contributions of enthalpy and entropy to the substituent, the following equations are used: $f_H = |\sigma_H|/|\sigma_H| + |\sigma_S|$, $f_S = |\sigma_S|/|\sigma_S| + |\sigma_H|$. It was observed that, in water at 25 °C, for the *meta*-hydroxy compound, the entropic contribution is equal to 80% of the total substituent effect, while for the *para*-hydroxy isomer, the enthalpic contribution ($f_H = 0.52$) prevails.

This clearly shows that the resonance contribution to the substituent effect for the *p*-OH isomer is larger than for the *m*-OH isomer. Indeed, the resonance effect is mainly related to the enthalpic term.

Thus, the β_i term in eqns. (4) and (5) influences the resonance effect by means of $\delta\Delta H_{in}$. This is not true for the m-OH derivative, for which the β_i and β_e parameters are equal, as commonly assumed.

It can therefore be concluded that statistical considerations are not in conflict with thermodynamic considerations.

The differences between the two theories can be ascribed to the fact that the same problem is considered by different points of view.

REFERENCES

1 L.P. Hammett, Physical-Organic Chemistry, 2nd edn., McGraw-Hill, New York, 1970.
2 J.E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, Wiley, New York, 1963.
3 L.G. Hepler, J. Am. Chem. Soc., 85 (1963) 3089.
4 J.W. Larson and L.G. Hepler, J. Org. Chem., 33 (1969) 3961.
5 J.W. Larson and L.G. Hepler, in J.F. Coetzee and C.D. Ritchie (Eds.), Solute–Solvent Interactions, Dekker, New York, 1963.
6 L.G. Hepler, Can. J. Chem., 49 (1971) 2804.
7 O. Exner, Collect. Czech. Chem. Commun., 38 (1973) 729.
8 T. Matzui, H.K. Ko and L.G. Hepler, Can. J. Chem., 52 (1974) 2906.
9 F. Rodante, Thermochim. Acta, 19 (1977) 13.
10 F. Rodante, G. Ceccaroni and M.G. Bonicelli, Thermochim. Acta, 42 (1980) 223.
11 F. Rodante, G. Ceccaroni and F. Fantauzzi, Thermochim. Acta, 59 (1982) 253.
12 F. Rodante, Thermochim. Acta, 56 (1982) 83.
13 F. Rodante, Thermochim. Acta, 57 (1982) 28.
14 F. Rodante, Thermochim. Acta, 57 (1982) 293.
15 F. Rodante, M.G. Bonicelli and G. Ceccaroni, Thermochim. Acta, 43 (1981) 199.