Thermodynamics of Benzoic Acid Protonation

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The thermodynamic parameters $\Delta G°$, $\Delta G_{T\text{hm}}$, $\Delta H°$, and $\Delta S°$ have been calculated using protonation constants for 12 *meta*- and *para*-substituted benzoic acids at 25, 40, and 60 °C and the van't Hoff model. The isokinetic temperature, β 327 K, was evaluated from regression analysis of the enthalpy and free energy estimates at the harmonic mean of the experimental temperatures (T_{hm} 314.17 K). The large difference between β and T_{hm} suggests a strong chemical compensation effect. The enthalpy, which is dominated by internal contributions, is comparable by an entropy contribution of equal sign to $\delta\Delta G°$. This finding essentially differs from the results for benzoic acid dissociation in water.

The acidity of benzoic acids have long been the subject of equilibrium measurements [1,2] as well as thermodynamic studies.[2–5] Only a few papers have investigated these systems as Brönsted bases [6–8] by comparisons of how substituents interact with the carbonyl group in these two equilibrium systems. Analysis of the thermodynamic properties of benzoic acids as Brönsted acids carried out with regard to the isokinetic relationship (this term hereinafter includes the isoequilibrium relationship) leads to values of β of -40 K[9] when the Exner statistical treatment [10] was applied to the pK_a measured at various temperatures, whereas β is 80 K[5] when the estimate was based chiefly upon calorimetrically measured enthalpies of reaction combined with pK_a values.

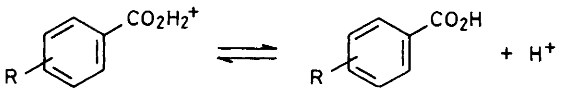
Isokinetic temperatures can now be determined with acceptable precision.[10,11] It was found [12] for ionic reactions that the isokinetic temperature reflects the importance of the $\delta\Delta H°$ contribution to $\delta\Delta G°$ and even the $\delta\Delta H°_{\text{int}}$[13] contribution to the overall change in free energy $\delta\Delta G° = 2.303RT.pK_a$. It is shown [12] that for reaction series with an isokinetic temperature with the requirement $|\beta/T| < 1$ the dominant contribution to $\delta\Delta G°$ comes from the change in entropy $\delta\Delta S°$, which in turn is due almost completely to external interactions (the Pitzer assumption).[14]

Benzoic acids regarded as Brönsted acids fall into this category. Thus the dominant contribution to $\delta\Delta G°$ is the entropy depending on solute–solvent interactions. It is important since benzoic acids have been chosen originally [15,16] to determine σ_R from σ_p and σ_I and hence σ_p should reflect the intramolecular substituent effect. If the reaction series do not obey the isokinetic relationship, the ratio $\delta\Delta H°/\delta\Delta S° = \beta$ varies from one member of the series to another and the blend of enthalpy and entropy contributions to $\delta\Delta G°$ is not constant and any conclusions about intramolecular interactions are in doubt.[12] This point is in line with Exner's statement [17] that an isokinetic relationship is a necessary condition for a simple l.f.e.r. to hold.

This work analyses the thermodynamic properties of benzoic acids regarded as Brönsted bases with particular interest in their isokinetic properties.

Results and Discussion

Table 1 presents data on the pK_{BH^+} values of *meta*- and *para*-substituted benzoic acids at 25, 40, and 60 °C for reaction (1). Thermodynamic parameters, $\Delta G°$, $\Delta G°_{T\text{hm}}$, $\Delta H°$, and $\Delta S°$, and their uncertainty were calculated using the van't Hoff model and harmonic mean temperature of the experiment (T_{hm} 314.17 K). Four acids, with R = H, *p*-I, *m*-Br, and *p*-NH_3^+, were omitted from further discussion of the isokinetic relationship and its chemical significance, due to the high uncertainty of $\Delta G°$ and $\Delta H°$.



(1)

To avoid the misleading and uncertain relation between $\Delta H°$ and $\Delta S°$, we used the procedure proposed by Krug.[11] The regression of enthalpy estimates on free energy estimates evaluated at the harmonic mean of the experimental temperature [as shown in (2)] was satisfactory. The slope equivalent

$$\delta\Delta H° = 5.365 - 0.510\ \delta\Delta G_{T\text{hm}}\ n\ 8,\ r\ 0.987 \qquad (2)$$

to $1/(1\text{-}T/\beta)$ yields the isokinetic temperature, β -327 K. The large difference of the isokinetic temperature and the harmonic mean of the experimental temperature suggests a strong chemical compensation effect. This is different from an earlier finding on dissociation of benzoic acids, where $\beta \sim 0$ K.[5,9]

The analysis of compensation effects is based on previous work by Krygowski and Guilleme.[12] The isokinetic temperature and the harmonic mean of the experimental temperature are of similar magnitude and opposite sign (thus $|\beta/T| \sim 1$), and hence $|\delta\Delta H°| \approx |T\delta\Delta S°|$, but since $\beta < 0$, $\delta\Delta H°$ and $\delta\Delta S°$ are opposite in sign. Another consequence of $\beta < 0$ is[12] that internal and external contributions to enthalpy, $\delta\Delta H_{\text{int}}$ and $\delta\Delta H_{\text{ext}}$, are opposite in sign, the first term being dominant. This simply means that the internal contribution to the substituent effect (measured by $\delta\Delta G°$) in benzoic acids as Brönsted bases is much more important than in benzoic acids as Brönsted acids, for which β is not well established [5,9] and close to 0 K. Therefore we conclude that the series under study is well suited to further analysis of substituent effects, with the purpose of studying its composition in terms of inductive and resonance effects.

The Dewar–Grisdale model [18] with substituent parameters *F* and *M* has been applied to experimental data at 25 °C. Table 2 shows the resulting transmission coefficients of inductive *a*, and resonance *b* effects for benzoic acids as Brönsted bases, and acids, for comparison.

The size of the transmission coefficient of the inductive effect *a* is slightly higher in the *meta*- than in the *para*-position in agreement with chemical intuition. Again, the mesomeric contribution is very important in the *para*-position and can be neglected in the *meta*-position. The blend of electronic effects in *para*-compounds as expressed by the ratio *a*/*b* is 3.82 and 3.74 for pK_{BH^+} and pK_a, respectively. However, it should be

Table 1. Basicity and thermodynamic parameters of benzoic acids

Substituent	$-pK^{25}_{BH^+}$	$-pK^{40}_{BH^+}$	$-pK^{60}_{BH^+}$	ΔG/kcal mol^{-1}	ΔG_{Thm}/kcal mol^{-1}	$\Delta H°$/kcal mol^{-1}	$\Delta S°$/cal K^{-1} mol^{-1}	r [a]	f [b]
p-OH	7.30 ± 0.05	6.90 ± 0.07	6.40 ± 0.10	13.4 ± 0.2	13.5 ± 0.2	11.7 ± 0.2	−5.8 ± 0.5	0.999	0.019
p-CH$_3$	7.52 ± 0.07	7.12 ± 0.10	6.65 ± 0.06	12.3 ± 0.1	12.4 ± 0.1	11.3 ± 0.1	−3.5 ± 0.2	0.999	0.006
m-CH$_3$	7.70 ± 0.10	7.31 ± 0.08	6.96 ± 0.07	8.7 ± 0.8	8.6 ± 0.8	9.6 ± 0.8	3.1 ± 2.5	0.997	0.116
H	7.93 ± 0.07	7.25 ± 0.10	6.97 ± 0.08	13.9 ± 3.6	14.0 ± 3.6	12.3 ± 3.6	−5.3 ± 11.5	0.959	0.400
p-F	7.80 ± 0.05	7.50 ± 0.08	7.27 ± 0.07	3.0 ± 0.9	2.9 ± 0.9	6.8 ± 0.9	12.7 ± 2.8	0.992	0.179
m-OH	8.08 ± 0.04	7.75 ± 0.05	7.25 ± 0.10	10.6 ± 0.9	10.6 ± 0.9	10.8 ± 0.9	0.8 ± 2.4	0.998	0.095
p-Cl	8.25 ± 0.06	7.91 ± 0.06	7.58 ± 0.11	6.1 ± 0.5	6.0 ± 0.5	8.7 ± 0.5	8.6 ± 1.6	0.998	0.084
p-I	8.00 ± 0.10	7.86 ± 0.06	7.41 ± 0.08	4.6 ± 1.9	4.4 ± 1.9	7.8 ± 1.9	10.8 ± 6.2	0.970	0.341
m-Cl	8.61 ± 0.11	8.07 ± 0.10	7.50 ± 0.08	17.0 ± 0.5	16.8 ± 0.5	14.4 ± 0.5	−8.9 ± 1.6	0.999	0.050
m-Br	8.67 ± 0.12	8.00 ± 0.08	7.70 ± 0.13	13.1 ± 3.4	13.2 ± 3.4	12.4 ± 3.4	−2.4 ± 1.7	0.964	0.374
p-CF$_3$	8.62 ± 0.10	8.15 ± 0.07	7.75 ± 0.08	10.8 ± 1.1	10.7 ± 1.1	11.2 ± 1.1	1.6 ± 3.5	0.995	0.137
p-NH$_3^+$	8.72 ± 0.12	8.12 ± 0.06	7.91 ± 0.11	8.9 ± 3.4	8.9 ± 3.4	10.3 ± 3.4	4.8 ± 10.9	0.949	0.447

[a] Correlation coefficient in the van't Hoff equation. [b] Inclination of a special regression line.

Table 2. Parameters of the Dewar–Grisdale model

	aF	+	bM	+	$pK°$	n [a]	r [b]
para							
$pK^{25}_{BH^+}$	$(-0.80 \pm 0.17)F$	−	$(0.21 \pm 0.04)M$	−	7.79 ± 0.10	5	0.990
pK^{25}_a	$(-0.51 \pm 0.04)F$	−	$(0.14 \pm 0.01)M$	+	4.20 ± 0.02	5	0.999
meta							
$pK^{25}_{BH^+}$	$(-1.16 \pm 0.06)F$	−	$(0.02 \pm 0.02)M$	−	7.90 ± 0.03	5	0.998
pK^{25}_a	$(-0.59 \pm 0.01)F$	+	$(0.00 \pm 0.02)M$	+	4.21 ± 0.01	5	1.000

[a] Number of compounds. [b] Correlation coefficient.

stressed that this ratio for benzoic acids as acids is somewhat less conclusive due to the ill defined $\beta^{5,9}$ which is close to 0 K. Further discussion of substituent effects on the basicity of benzoic acids is desirable. For this reaction electronic contributions are more reliable due to the conditions $\beta < 0$ and $|\beta/T| \sim 1$.

Experimental

Protonation was followed by the u.v. spectrophotometric method. The resulting family of absorption curves were used for calculations of pK_{BH^+} by the c.v.a.-t.c.a. method.[19] The absorption was measured by Specord u.v.-visible and Cary M-14 spectrophotometers in the range 200–400 nm in cells thermostatted at 25, 40, and 60 ± 0.2 °C. Samples for absorption measurements (5×10^{-5}M) were prepared from stock solutions in methanol. Methanol was evaporated before dissolving the solute in sulphuric acid. The H_0 acidity function at normal and elevated temperatures was used.[20] For each compound two independent runs were performed, each consisting of 12—15 measurements.

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