Thermodynamics of Ionization of Aqueous Methoxy Phenols

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Heats of ionization of o-methoxy phenol, *m*-methoxy phenol and *p*-methoxy phenol in aqueous solution have been determined calorimetrically. Combination of our results with ΔF° values from ionization constants gives ΔS° values for ionization of these substituted phenols in aqueous solution. Interpretation of the thermodynamic data in terms of resonance and inductive effects and solute-solvent interactions is discussed briefly.

THIS INVESTIGATION of the thermodynamics of ionization of aqueous methoxy phenols was undertaken as a continuation of a program to accumulate such data for a variety of organic acids. The methoxy phenols were chosen largely because *m*-methoxy phenol is a stronger acid than phenol while *p*-methoxy phenol is a weaker acid than phenol.

EXPERIMENTAL

The calorimeter used is patterned after one previously described (*5*), except that a Mueller G-2 Bridge and HS galvanometer were used with a nickel wire resistance thermometer for temperature measurements. All of the calorimetric work reported here was carried out with 950 ml. of H_2O or solution in the calorimeter at 25.0 ± 0.1° C.

Eastman Organic Chemicals were purified by distilling them twice in all glass apparatus at reduced pressure. The ortho and meta methoxy phenols were distilled at 107–110° C. and the *p*-methoxy phenol at 72° C. Only the middle portions of second distillates were used for calorimetric runs. The *p*-methoxy phenol melted at 53° C.

Sodium hydroxide solution was prepared and standardized by common procedures.

RESULTS AND CALCULATIONS

Heats of ionization were determined by measuring the heats of neutralization of aqueous methoxy phenols with concentrated NaOH solutions. Ten ml. aliquots of 4.946 *M* NaOH were reacted with 950 ml. of water containing a known amount of methoxy phenol in solution. A general reaction equation for this process is:

$$\mathrm{HA(aq.) + OH^-(conc.) = A^-(aq.) + H_2O(liq.)}$$

Separate determination of the total heat associated with breaking the bulb containing the NaOH and diluting the NaOH permitted us to calculate ΔH for the reaction:

$$\mathrm{HA(aq.) + OH^-(aq.) = A^-(aq.) + H_2O(liq.)}$$

These values, designated ΔH_n, are listed in Tables I, II, and III. Combination of these heats of neutralization with ΔH° = 13,500 cal./mole for the heat of ionization of water (*6*) leads to the heats of ionization (ΔH_i°) for:

$$\mathrm{HA(aq.) = H^+(aq.) + A^-(aq.)}$$

that are listed in Table IV with free energies and entropies of ionization. The free energies were calculated from the p*K* values listed by Kortum, Vogel, and Andrussow (*4*). Similar data for aqueous phenol are also listed (*1*).

Table I. Heats of Neutralization of o-Methoxy Phenol

Moles *o*-MP/950 Ml.	$-\Delta H_n$(Kcal./Mole)
0.007692	7.77
0.009750	7.74
0.010826	7.73
0.015106	7.73
0.016758	7.72
0.018629	7.75
0.018842	7.75

DISCUSSION

The ionization constants and free energies of ionization of *m*-methoxy phenol and *p*-methoxy phenol relative to phenol have been explained on the basis that the inductive effect of the methoxy group in the meta position makes it "easier" to remove a proton while resonance stabilization of the un-ionized acid outweighs the inductive effect in *p*-methoxy phenol and makes this compound a weaker acid than phenol. This explanation is based on consideration of energy effects within the acid molecules and their anions (ΔH_{int}) and implicitly assumes that entropy and solute-solvent interactions (ΔS° and ΔH_{ext}) do not contribute to differences in the free energy of ionization. Since ΔS_i° values for phenol and *m*-methoxy phenol are nearly the same and since equal entropies of ionization for similar acids indicate that solute-solvent interactions are nearly

Table II. Heats of Neutralization of *m*-Methoxy Phenol

Moles *m*-MP/950 Ml.	$-\Delta H_n$(Kcal./Mole)
0.006034	8.24
0.008598	8.22
0.010039	8.22
0.010166	8.20
0.011640	8.25
0.016518	8.19
0.017490	8.22

Table III. Heats of Neutralization of *p*-Methoxy Phenol

Moles *p*-MP/950 Ml.	$-\Delta H_n$(Kcal./Mole)
0.005727	7.79
0.007503	7.75
0.010454	7.81
0.010831	7.80
0.012185	7.75
0.013301	7.76
0.014667	7.77
0.015385	7.75

Table IV. Thermodynamics of Ionization of Phenol and Methoxy Phenols

Acid	ΔF_i° (Kcal./Mole)	ΔH_i° (Kcal./Mole)	ΔS_i° (Cal./Deg. Mole)
Phenol	13.61	5.65	−26.7
o-Methoxy phenol	13.63	5.74	−26.5
m-Methoxy phenol	13.17	5.26	−26.5
p-Methoxy phenol	13.92	5.70	−27.6

equal (3, 7), the above explanation is satisfactory for *m*-methoxy phenol.

Only 50 cal./mole of 310 cal./mole difference in ΔF_1° values for phenol and *p*-methoxy phenol are accounted for by ΔH_1° values. We therefore conclude that the ΔH_{int} effect related to resonance stabilization of un-ionized *p*-methoxy phenol is obscured by effects of solute-solvent interactions on ΔH_{ext} and ΔS°. We may separate all these contributions to the free energy of ionization by following earlier work (2, 3) and considering a reaction:

$$\text{HAx(aq.)} + \text{A}^-\text{(aq.)} = \text{Ax}^-\text{(aq.)} + \text{HA(aq.)} \qquad (1)$$

for which the equation:

$$\Delta H_{\text{int}} = \Delta H_1^{\circ} - 280\ \Delta S_1^{\circ}$$

has been obtained (2, 3). Using data for phenol and *p*-methoxy phenol from Table IV in this equation gives $\Delta H_{\text{int}} = +300$ cal./mole for *p*-methoxy phenol in reaction (*1*), thus showing that resonance stabilization makes it energetically "harder" to remove a proton from *p*-methoxy phenol than from phenol.

The free energy change ΔF_1° for *p*-methoxy phenol in reaction (*1*) is 310 cal./mole, so $\Delta F_1^{\circ} \cong \Delta H_{\text{int}}$ because of the almost equal contributions of ΔH_{ext} and $T\Delta S_1^{\circ}$ to $\Delta F_1^{\circ\,2}$. Similarly, ΔF_1° equals −440 and +20 cal./mole while ΔH_{int} equals −450 and +30 cal./mole for *m*-methoxy phenol and *o*-methoxy phenol, respectively, in reaction (*1*).

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Thermodynamics of Solutions XI. Heats of Mixing of Hydrocarbons

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A calorimeter, designed to combine convenience and quick operation with reasonable accuracy, allows the measurements of four heats of mixing in a single run. The comparison of some of the results with good literature values indicates that the probable error is less than 1%. Data for 27 binary hydrocarbon systems at 25° and 50° C. are better represented as a function of the volume fraction than as a function of the mole fraction.

AN EXTENSIVE, SYSTEMATIC BODY of heats of mixing data is an essential precursor to the formulation of any precise rules for predicting solution behavior. Hydrocarbon mixtures have been chosen as the first step in a program designed to contribute to this growing body of data.

In addition to accuracy, the critical design requirements for a mixing calorimeter are the amount of material used and the time required for the operation. Since it was necessary to cover a wide field, operation time was important. The calorimeter, therefore, allows the determination of the heat of mixing at four concentrations (0–50%) in a single run. A total volume of 45 ml. was considered tolerable since neither work with expensive materials nor unusually difficult purifications was anticipated. Except for accidental failure, two sets of measurements (two fillings, two days of work) are sufficient to describe the excess heat content of a mixture at a single temperature over the whole concentration range, except for possible anomalies at high dilutions. A few measurements with large amounts of materials are believed to be better than numerous determination with small amounts. With a volume of 45 ml., the vaporization correction, if properly computed, is not believed to depress the upper limit of the temperature range excessively. The uncertainty of this correction of 50° C. is less than the desired limits of error (about 1%).

CALORIMETER

The stirrer, *k*, (Figure 1) contains four compartments of 5 ml. each. They are formed by a shell of the shape of an inverted cup (cylinder and cone), and by four vertical dividers. A thin metal foil (usually tin, 0.02 mm.), secured at the bottom of the four compartments by a ring and crossbars pressing on the dividers, closes the compartments. One turn of a screw thread at the outside of the cylindrical part stiffens the shell and assists in stirring.

When the stirrer is depressed by means of the knurled knob, *b*, the foil isolating the appropriate compartment is ruptured against the sawblade, *n*, and the components are allowed to mix. Normally, the stirrer with its four compartments rotates at 200 r.p.m. and it is necessary to stop stirring in order to rupture the foil. This takes about five seconds. Fortuitously, the heat of rupture is for all