Thermodynamics of Ionization
of Aqueous Hydroxybenzaldehydes and Vanillins

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Heats of ionization of o-hydroxybenzaldehyde, m-hydroxybenzaldehyde, p-hydroxy-benzaldehyde, vanillin, isovanillin and o-vanillin have been determined calorimetrically at 298°K. Entropies of ionization of these acids in aqueous solution have been calculated from these heats and free energies derived from ionization constants. The thermodynamic data are discussed briefly.

THIS INVESTIGATION of the thermodynamics of ionization of aqueous hydroxybenzaldehydes and vanillins was undertaken as part of a program aimed at the determination of such data for a variety of substituted phenols. These particular compounds have been investigated because of their relevance to eventual understanding of the additivity (nonadditivity for some combinations) of substituent effects on acidity of phenols. Results of similar investigations of methoxyphenols have been reported recently (2).

EXPERIMENTAL

The calorimeter used is patterned after one previously described (3), except that a Mueller G-2 bridge and HS galvanometer were used with a nickel wire resistance thermometer for temperature measurement. Also, the resistance thermometer and calibration heater were contained in a glass coil filled with mineral oil rather than would on a silver cylinder. All the calorimetric work reported here was carried out with 950 ml. of H_2O or appropriate solution in the calorimeter at 25.0 ± 0.1° C.

o-Hydroxybenzaldehyde and vanillin (both from Fisher Scientific Co.) were distilled under reduced pressure twice in an all glass apparatus. Only the middle portions of the second distillates were used in the calorimetric runs. m-Hydroxybenzaldehyde (from Aldrich Chemical Co.), isovanillin and o-vanillin (both from Cal-Bio-Chem) were purified in the same way. p-Hydroxybenzaldehyde (from Fisher Scientific Co.) was purified by sublimation under reduced pressure.

The sodium salt of o-vanillin was prepared by adding purified o-vanillin to a solution of NaOH in absolute ethanol. The resulting salt was recrystallized from 95% ethanol and washed with absolute ethanol. It was then dried and stored for future use.

HCl and NaOH solutions were prepared and standardized by common procedures.

RESULTS AND CALCULATIONS

Heats of ionization were determined by measuring the heats of reaction of aqueous phenols with aqueous NaOH. Ten ml. aliquots of 4.946M NaOH were caused to react with 950 ml. of H_2O containing a known amount of substituted phenol. A general reaction equation for this process is:

$$HA(aq.) + OH^-(conc.) = A^-(aq.) + H_2O(liq.)$$
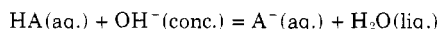
Separate determinations of the total heat associated with breaking the bulb containing the NaOH and diluting the NaOH permitted us to calculate heats for the reactions:

$$HA(aq.) + OH^-(aq.) = A^-(aq.) + H_2O(liq.)$$
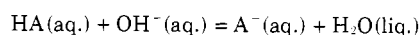
These values, designated ΔH_n, are listed in Tables I-V. Combination of these heats of neutralization with $\Delta H° = 13.50$ kcal. mole^{-1} for the heat of ionization of water (4) leads to the desired heats of ionization $\Delta H°$ for:

$$HA(aq.) = H^-(aq.) + A^-(aq.)$$
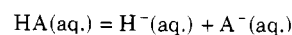
These heats of ionization are listed in Table VIII, along with free energies and entropies of ionization. The free energies were calculated from pK values from references cited in Table VIII.

Because of solubility difficulties with o-vanillin, it proved easier to determine the heat of ionization of this compound by measuring the heats of solution of the sodium salt in acidic and basic solutions. The calorimetric reaction equation for solution in very dilute NaOH (to prevent hydrolysis) is:

$$NaA(c) = A^-(aq.) + Na^-(aq.)$$
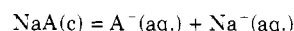
and the experimental results, designated ΔH_1, are listed in

Table I. Heats of Neutralization of o-Hydroxybenzaldehyde

Moles o-OH-ϕCHO/950 ml.	$-\Delta H_n$ (Kcal. Mole^{-1})
0.005045	8.35
0.007596	8.34
0.008963	8.35
0.010816	8.34
0.011229	8.36
0.011774	8.36

$\Delta H_n° = -8.35$ kcal. mole^{-1}

Table II. Heats of Neutralization of m-Hydroxybenzaldehyde

Moles m-OH-ϕCHO/950 ml.	$-\Delta H_n$ (Kcal. Mole^{-1})
0.004265	8.33
0.005515	8.32
0.006304	8.34
0.007293	8.32
0.008545	8.33
0.009122	8.32

$\Delta H_n° = -8.33$ kcal. mole^{-1}

Table III. Heats of Neutralization of p-Hydroxybenzaldehyde

Moles p-OH-ϕCHO/950 ml.	ΔH_n (Kcal. Mole^{-1})
0.005267	9.23
0.006912	9.25
0.007339	9.24
0.007540	9.22
0.008699	9.24
0.009692	9.22
0.010989	9.23
0.011626	9.24

$\Delta H_n^{\circ} = -9.24$ kcal. mole^{-1}

Table IV. Heats of Neutralization of Vanillin

| Moles Vanillin/950 ml.	$-\Delta H_n$(Kcal. Mole^{-1})
0.003806	9.74
0.006476	9.73
0.006942	9.71
0.007754	9.70
0.008937	9.72
0.010586	9.69

$\Delta H_n^{\circ} = -9.75$ kcal. mole^{-1}

Table V. Heats of Neutralization of Isovanillin

Moles Isovanillin/950 ml.	$-\Delta H_n$(Kcal. Mole^{-1})
0.004459	8.92
0.005104	8.84
0.005783	8.88
0.005960	8.89
0.006476	8.90
0.007208	8.91
0.007619	8.85

$\Delta H_n^{\circ} = -8.88$ kcal. mole^{-1}

Table VI. Heats of reaction of the sodium salt of o-vanillin with dilute HCl as in the equation:

$$NaA(c) + H^-(aq.) = HA(aq.) + Na^-(aq.)$$
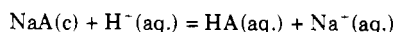
were also measured. Results of these measurments, designated ΔH_2, are listed in Table VII. The desired heat of ionization of aqueous o-vanillin has been calculated as $\Delta H_1^{\circ} - \Delta H_2^{\circ}$, and is listed in Table VIII with the free energy and entropy of ionization.

EXPERIMENTAL

The data in Table VIII for o-methoxyphenol and phenol show that the effect of an o-CH$_3$O group on thermodynamics of ionization is small. If substituent effects are entirely additive for the groups under discussion, we should there-

Table VI. Heats of Solution of Na$^+$ Salt of o-Vanillin

Moles Salt/950 Ml.	ΔH_1(Kcal. Mole^{-1})
0.003485	1.39
0.004705	1.45
0.005777	1.42
0.007201	1.43
0.007977	1.46

$\Delta H_1^{\circ} = 1.37$ kcal. mole^{-1}

Table VII. Heats of Reaction of Na$^+$ Salt of o-Vanillin with H$^+$(aq.)

Moles Salt/950 Ml.	$-\Delta H_2$(Kcal. Mole^{-1})
0.004203	2.77
0.005732	2.74
0.005753	2.76
0.006424	2.74
0.009556	2.77

$\Delta H_2^{\circ} = -2.76$ kcal. mole^{-1}

fore expect ΔF°, ΔH° and ΔS° of ionization values for the hydroxybenzaldehydes and the vanillins with the CHO group in similar positions to be nearly the same. The data in Table VIII show that neither ΔF° nor ΔH° values are additive, with the deviations from additivity being only about half as much for ΔF° values for ΔH° values.

Detailed discussion of additivity of substituent effects on thermodynamics of ionization of phenols will be given in a subsequent paper, along with thermodynamic data for ionization of di- and trisubstituted phenols.

ACKNOWLEDGMENT

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(6) Ibid., 52, 327 (1956).

Table VIII. Thermodynamics of Ionization of Phenol and Substituted Phenols

Substance	ΔF° (Kcal. Mole^{-1})	ΔH° (Kcal. Mole^{-1})	ΔS°(Cal. Mole^{-1} Deg.$^{-1}$)
Phenol	13.64	5.65	−26.7
o-Methoxyphenol	13.63	5.74	−26.5
m-Methoxyphenol	13.17	5.26	−26.5
p-Methoxyphenol	13.92	5.70	−27.6
o-Hydroxybenzaldehyde	11.42(6)	5.15	−21.0
m-Hydroxybenzaldehyde	12.31(6)	5.17	−23.9
p-Hydroxybenzaldehyde	10.39(6)	4.26	−20.6
o-Vanillin	10.79(5)	4.13	−22.3
Isovanillin	12.13(5)	4.62	−25.2
Vanillin	10.09(5)	3.75	−21.3

Thermodynamic data for ionization of aqueous phenol (1) and methoxyphenols (2) are listed in Table VIII for comparison.