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Note

Ionization of aqueous tropolone

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In our continuing study of weak acids in aqueous solution we have determined the thermodynamic ionization constant and standard heat of ionization of aqueous tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one).

The thermodynamic ionization constant was determined using benzoic acid-sodium benzoate as the buffer system with a method that has been described[1].

The first calorimeter at the Naval Academy was modified by substituting a Fluke Model 382A voltage–current calibrator in the calorimeter heater circuit, thereby eliminating the need for determining the current passing through the heater during calorimeter calibration periods[2,3]. Also, a Hewlett-Packard Model 5216A electronic counter was used as the timer in the heater circuit, allowing us to measure heating periods to ± 0.01 sec. The calorimeter[4] at Lethbridge is an LKB Model 8700 solution-reaction calorimeter.

The standard free energy of ionization of tropolone is calculated from our value of $pK_a = 6.88$ at 298 K to be $\Delta G^\circ_{ion} = 9387$ cal mol^{-1}.

Heats of neutralization of aqueous tropolone, 12 runs, by concentrated (2.0 M) NaOH solution were measured according to

$$\mathrm{TropH(aq.)} + \mathrm{OH^-(conc.)} = \mathrm{Trop^-(aq.)} + \mathrm{H_2O(l)}\ Q_n \qquad (1)$$

Separate measurements of the heat (Q_B) of breaking the frangible glass bulb containing the NaOH solution and dilution of this solution were made. Then the molar heat of neutralization of the aqueous tropolone is obtained from

$$\Delta H_n = (Q_n - Q_B)/(\text{moles tropolone}) \qquad (2)$$

These values of ΔH_n were extrapolated to infinite dilution to obtain the standard heat of neutralization $\Delta H^\circ = -10.87$ kcal mol^{-1}. Combining ΔH°_n with $\Delta H^\circ = 13.34$ kcal mol^{-1} for the standard heat of ionization of water[5] gives the desired standard heat of neutralization as $\Delta H^\circ_{ion} = 2.47$ kcal mol^{-1} for the reaction represented by

$$\mathrm{TropH(aq.)} = \mathrm{H^+(aq.)} + \mathrm{Trop^-(aq.)} \qquad (3)$$

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Combination of ΔH°_{ion} with ΔG°_{ion} gives $\Delta S^\circ_{ion} = -23.2\ \text{cal K}^{-1}\ \text{mol}^{-1}$ for the standard entropy of ionization.

All the thermodynamic properties for ionization of aqueous tropolone are intermediate between the corresponding properties[5] for ionization of aqueous benzoic acid and aqueous phenol, as might be expected on the basis of structure.

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