
Note

Ionization of aqueous tropolone

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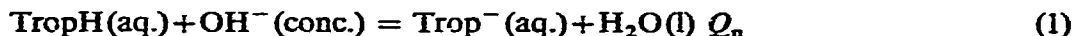
In our continuing study of weak acids in aqueous solution we have determined the thermodynamic ionization constant and standard heat of ionization of aqueous tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one).

The thermodynamic ionization constant was determined using benzoic acid-sodium benzoate as the buffer system with a method that has been described¹.

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 calorimeter⁴ 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 $\Delta G_{ion}^\circ = 9387 \text{ cal mol}^{-1}$.

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



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

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

These values of ΔH_n were extrapolated to infinite dilution to obtain the standard heat of neutralization $\Delta H^\circ = -10.87 \text{ kcal mol}^{-1}$. Combining ΔH_n° with $\Delta H^\circ = 13.34 \text{ kcal mol}^{-1}$ for the standard heat of ionization of water⁵ gives the desired standard heat of neutralization as $\Delta H_{ion}^\circ = 2.47 \text{ kcal mol}^{-1}$ for the reaction represented by



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Combination of $\Delta H_{\text{ion}}^{\circ}$ with $\Delta G_{\text{ion}}^{\circ}$ gives $\Delta S_{\text{ion}}^{\circ} = -23.2 \text{ cal K}^{-1} \text{ mol}^{-1}$ for the standard entropy of ionization.

All the thermodynamic properties for ionization of aqueous tropolone are intermediate between the corresponding properties⁵ for ionization of aqueous benzoic acid and aqueous phenol, as might be expected on the basis of structure.

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