

Studies on the Application of the Quinhydrone Electrode in Formamide. VII* The Ionization Constants and Related Thermodynamic Quantities of (E)-Cinnamic Acid from E.M.F. Measurements at Different Temperatures

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Abstract

The e.m.f. of the cell



(where HA is cinnamic acid) in formamide has been measured at 5° intervals over the temperature range 5-45°C. The pK_a value of (E)-cinnamic acid ranges from 7.02 ± 0.03 at 5° to 6.78 ± 0.05 at 45°.

Introduction

In previous communications,¹⁻⁶ the electrode Pt|Q-QH₂ in conjunction with the silver-silver chloride electrode has been successfully employed in the accurate determination of the ionization constant of acids in formamide by the e.m.f. method. In the present investigation, with this electrode, the cell



(where HA is cinnamic acid) has been studied in formamide at 5° intervals over the temperature range 5-45°C with a view to determining the ionization constant of (E)-cinnamic acid in this solvent.

Experimental

Cinnamic acid (Bush, England) was recrystallized thrice from hot water and the crystals were dried in a bottle through which dry, purified air was passed. Its purity was checked by titration.

Sodium cinnamate was prepared by adding the calculated quantity of sodium carbonate (B.D.H., AnalaR) to the known weight of pure cinnamic acid, evaporating the solution to dryness on the steam bath, and recrystallizing the product from 95% alcohol. The salt was dried at 110-120° for at least 2 h and kept in a vacuum desiccator over calcium chloride until required. Sodium chloride (B.D.H., AnalaR) was dried above 100° for 2 h before use. Formamide (Reidel, pure) was further purified as described earlier.⁷

* Part VI, *Aust. J. Chem.*, 1975, 28, 1653.

¹ Nayak, B., and Dash, U. N., *Aust. J. Chem.*, 1973, 26, 111.

² Nayak, B., and Dash, U. N., *Aust. J. Chem.*, 1973, 26, 115.

³ Dash, U. N., and Nayak, B., *Aust. J. Chem.*, 1975, 28, 793.

⁴ Dash, U. N., and Nayak, B., *Aust. J. Chem.*, 1975, 28, 797.

⁵ Dash, U. N., and Nayak, B., *Aust. J. Chem.*, 1975, 28, 1649.

⁶ Dash, U. N., *Aust. J. Chem.*, 1975, 28, 1653.

⁷ Dash, U. N., and Nayak, B., *Indian J. Chem.*, 1970, 8(7), 659.

Solutions for e.m.f. measurements were prepared by dissolving the appropriate weighed amounts of salts and acid in known weights of formamide.

The cell measurements were carried out with electrodes prepared and set up as described earlier.¹

Results and Discussion

The results of the e.m.f. measurements of the cell at 25° together with other data are presented in Table 1. Similar experimental values were obtained at other temperatures. The reproducibility was of the order of 0.2 mV.

Table 1. Determination of $-\log K_a$ of (*E*)-cinnamic acid in formamide at 25°C

$$X \equiv E - E^0(\text{Ag-AgCl}) + E^0(\text{QH}_2\text{-Q})$$

$10^2 m_1$ (mol/kg)	$10^2 m_2$ (mol/kg)	$10^2 m_3$ (mol/kg)	$-E$ (V)	$\frac{XF}{2 \cdot 303 RT}$	$-\log \frac{m_1 m_3}{m_2}$	$10^2 \mu$	$-\log K'_a$
0.396	0.346	0.852	-0.0085	8.859	2.0114	1.198	6.8476
0.312	0.482	1.242	-0.0120	8.919	2.0956	1.724	6.8234
0.724	0.420	1.762	0.0235	8.320	1.5177	2.182	6.8023
1.969	0.438	3.727	0.0644	7.628	0.7756	4.165	6.8524
0.595	0.836	3.631	0.0220	8.345	1.5876	4.467	6.7574
1.300	0.539	4.606	0.0580	7.736	0.9542	5.145	6.7818
1.345	0.541	6.564	0.0697	7.539	0.7870	7.105	6.7520
1.476	0.530	6.831	0.0731	7.480	0.7206	7.361	6.7594
0.102	0.306	7.657	0.0240	8.312	1.5929	7.963	6.7191
$-\log K_a$ (extrapolated)							6.86 ± 0.02

As usual,^{1,8} values of K'_a were calculated with the help of equation (1):

$$\begin{aligned}
 -\log K'_a &= [E - E^0(\text{Ag-AgCl}) + E^0(\text{QH}_2\text{-Q})]F/2 \cdot 303 RT + \log(m_1 m_3 / m_2) \\
 &= -\log K_a - \log[\gamma(\text{Cl}^-) \cdot \gamma(\text{HA}) / \gamma(\text{A}^-)]
 \end{aligned} \quad (1)$$

and the ionization constant, K_a , was found by the method^{1,8} of extrapolating the auxiliary function $-\log K'_a$ to zero ionic strength, as $\log[\gamma(\text{Cl}^-) \cdot \gamma(\text{HA}) / \gamma(\text{A}^-)]$ tends to zero. The symbols in equation (1) have their usual significance.

The values of $E^0(\text{Ag-AgCl})$ and $E^0(\text{QH}_2\text{-Q})$ at different temperatures needed for the calculations were obtained as described earlier.³

The $\text{p}K_a$ values of (*E*)-cinnamic acid at different temperatures in formamide are

5°	7.02 ± 0.03	20°	6.90 ± 0.02	35°	6.76 ± 0.05
10°	6.93 ± 0.06	25°	6.86 ± 0.02	40°	6.89 ± 0.09
15°	6.93 ± 0.04	30°	6.79 ± 0.03	45°	6.78 ± 0.05

Considering experimental difficulty inherent in such work the accuracy appears reasonable.

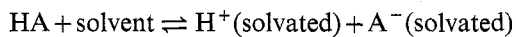
A comparison of the present data with the corresponding values in water is difficult because of the lack of relevant data in water at all temperatures. However, available data at a single temperature, i.e. at 25° in water⁹ (4.44), show that the $\text{p}K_a$ value in formamide (6.86 at 25°) is higher than in water—a behaviour similar to that shown by weak acids in solvents of this class.^{1-6,8,10}

⁸ Dash, U. N., and Nayak, B., *Aust. J. Chem.*, 1972, **25**, 941.

⁹ Albert, A., and Serjeant, E. P., 'Ionization Constants of Acids and Bases' p. 124 (Methuen: New York 1962).

¹⁰ Dawson, L. R., Vaughn, J. W., Pruitt, M. E., and Eckstrom, H. C., *J. Phys. Chem.*, 1962, **66**, 2684.

The effect of temperature on pK_a values appears to be irregular, although with the increase of temperature there is a general tendency for these values to decrease slightly. The standard free energy change, ΔG° , of the ionization process



was calculated from $\Delta G^\circ = -RT \ln K_a$, and found to be 39140 J at 25°.

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