Journal of Fluorine Chemistry, 8 (1976) 447–450
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Received: April 13, 1976

SHORT COMMUNICATION

Studies on N-p-tolyl-p-fluorobenzohydroxamic acid : Thermodynamic ionisation constants

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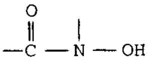
Hydroxamic acids, with the functional grouping,  $-\overset{O}{\overset{\|}{C}}-\overset{|}{N}-OH$ are the versatile reagents for inorganic and organic analyses [1—5]. They react with metal ions and form five membered ring complexes. So far no data are available on the physico-chemical properties of the fluorosubstituted hydroxamic acids. Therefore, it is desirable to determine the thermodynamic ionisation constants of N-p-tolyl-p-fluorobenzohydroxamic acid for its rational analytical applications.

The sample titration data on N-p-tolyl-p-fluorobenzohydroxamic acid are given in Table 1. The thermodynamic ionisation constants (pK_a) at different mole fraction of dioxane at 25° and 35° are given in Table 2. The plots of pK_a vs mole fraction of dioxane at a given temperature is linear. The pK_aS do not vary linearly with the reciprocal of dielectric constant. The empirical relation $pK_a = mn_2 + C$ is obtained by the method of least squares and relevant correlation coefficients are also given in Table 2. It is believed that the pK_a values reported are accurate to $\pm$ 0.03 unit. The thermodynamic parameters for N-p-tolyl-p-fluorobenzohydroxamic acid are summarised in Table 3.

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TABLE 1

Thermodynamic ionisation constants of N-p-tolyl-p-fluorobenzohydroxamic acid in 50%, v/v dioxane water media at 25°

Concentration: 0.0.1 M at half neutralization [10] N-p-tolyl-p-fluorobenzohydroxamic acid (0.12263 g) was dissolved in dioxane (23.75 ml) and water (23.75 ml).

$\log U^{o}_{H} = 0.20$ [11]

Titrant TBAH 0.1000 M (ml)	B B	$[HA]$ mole l^{-1}	$[A^-]$ mole l^{-1}	$\log 1/y_{\pm}$ [12]	pK_a
0.00	7.35	0.01	-	-	10.99
0.50	9.80	0.009	0.001	0.038	10.99
1.00	10.13	0.008	0.002	0.070	11.00
1.50	10.32	0.007	0.003	0.097	10.99
2.00	10.50	0.006	0.004	0.109	10.98
2.50	10.66	0.005	0.005	0.119	10.98
3.00	10.85	0.004	0.006	0.128	11.00
3.50	11.03	0.003	0.007	0.134	11.00
4.00	11.25	0.002	0.008	0.143	10.99
4.50	11.50	0.001	0.009	0.150	10.99
5.00	12.01	-	-	-	-

$$pK_a = B + \log \frac{[HA]}{[A^-]} + \log U^{o}_{H} + \log 1/y_{\pm}$$

Result: Average $pK_a = 10.99 \pm 0.02$

Where B is the pH meter reading, $\log U^{o}_{H}$ is conversion factor at zero ionic strength [11, 13] and $y_{\pm}$ is mean activity coefficient, interpolated from the data of Harned and Owen [12] for desired dioxane water media.

Preparation of N-p-tolyl-p-fluorobenzohydroxamic acid

In three necked flasks (500 ml) equipped with a stirrer, dropping funnel, and thermometer, diethyl ether (150 ml), freshly crystallized N-p-tolylhydroxylamine (12.3 g) and a fine suspension of sodium bicarbonate (12.6 g) in water (25 ml) were added. After the mixture was cooled to 0°C, p-fluorobenzoyl chloride (15.8 g), dissolved in diethyl ether (100 ml), was added dropwise over a period of 1 h. Then an additional time of 30 min was allowed and the temperature was maintained at 0°C or lower. A white solid was precipitated while the ether layer was separated and the ether removed under vacuum. The light yellow residue was combined with the precipitated white

TABLE 2

Thermodynamic ionisation constants of N-p-tolyl-p-fluorobenzohydroxamic acid

v/v % dioxane	n_2, mole fraction of dioxane	Dielectric constant [12]	pK_a (25°)	pK_a (35°)
10	0.023	68.5	9.04	8.93
20	0.050	60.5	9.39	9.28
30	0.083	51.8	9.81	9.70
40	0.123	42.5	10.32	10.21
45	0.147	37.5	10.63	10.52
50	0.174	33.0	10.99	10.88
60	0.240	23.95	11.81	11.70
70	0.330	16.50	12.96	12.85

At 25° $pK_a = 12.76\, n_2 + 8.75$

At 35° $pK_a = 12.76\, n_2 + 8.64$

The correlation coefficient is 0.99 and 0.997 at 25° and 35° respectively.

solid, triturated for about 15 min in a procelain mortar with a saturated solution of sodium bicarbonate to remove the acid impurities, filtered and washed with cold water. The yield of air dried product, m.p. 136° was 76%. Two crystallizations from a mixture of benzene and petroleum ether without the use of charcoal gave white needles, m.p. 138°, reported 138° [6]. Analysis: Found C, 68.77; H, 5.83%. $C_{14}H_{12}NO_2F$ requires C, 68.55; H, 4.93 N, 5.7%.

TABLE 3

Thermodynamic parameter [14] on N-p-tolyl-fluorobenzohydroxamic acid

Dioxane % , v/v	Δ G° (kcal/mol) 25°	Δ G° (kcal/mol) 35°	ΔS° (cal/mol) 25°	ΔS° (cal/mol) 35°
10	12.37	12.60	26.06	25.95
20	12.84	13.09	27.64	27.54
30	13.42	13.69	29.58	29.49
40	14.11	14.41	31.90	31.82
45	14.54	14.85	33.31	33.25
50	15.04	15.36	35.02	34.91
60	17.73	18.13	44.02	43.89

$\Delta H^{\circ} = 4.6$ kcal/mole

p-Dioxane was purified by the procedure of Weissberger [7]. Glass distilled water was redistilled over alkaline permanganate. It was tested for the absence of carbonate by the method of Kolthoff [8]. Tetrabutyl ammonium hydroxide was used as a titrant and was further purified by the method of Kundiff and Markunas [9] and diluted to 0.1 N with dioxane.

A Radiometer pH meter, equipped with a glass electrode and calomel electrode was used for pH measurement. The meter is claimed to be accurate ± 0.01 pH unit.

The titration procedure was essentially that recommended by Albert and Serjeant [10]. N-p-tolyl-p-fluorobenzohydroxamic acid (0.01 mol in 50 ml solvent) was placed in a three necked titration vessel (thermostated at 25^{o} or 35^{o}) carrying a glass electrode, calomel electrode and microburette. Nitrogen gas presaturated with solvent was passed through the solution which was titrated with an aliquots (0.5 ml) tetrabutyl ammonium hydroxide, TBAH, (0. 1 ml) noting the highest appropriate drift free reading on the pH meter.

We would like to thank Prof. H.J. Emeleus, University Chemical Laboratory, Cambridge, for valuable suggestions and critism.

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