

Note

Electromigration of carrier-free radionuclides

IX. Protolysis of [^{131}I]iodate in aqueous solutions

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(First received July 15th, 1988; revised manuscript received September 8th, 1988)

In addition to the hydrolysis and complex formation equilibria of metal cations, protolysis reactions of oxoanions can also be investigated by means of electrophoretic methods. In particular, for amino acids, carboxylic acids and dipeptides isotachophoretic methods have yielded $\text{p}K_a$ data^{1–3}. Electrochromatography on paper⁴ and quartz powder⁵ has also been used to study the dissociation equilibria of phenols, aromatic amines, amino acids and carboxylic acids.

It was the aim of this work to demonstrate the possibilities of a modified version of the electromigration method in electrolyte solutions free from any supporting materials. A chemical system was chosen for which the application of other analytical methods had yielded many representative data on the protolysis constant, but for which no data had been obtained by means of the electromigration technique. The protolysis of the iodate anion satisfies both criteria. Table I summarizes the $\text{p}K_a$ values of iodate published up to 1976^{6,7}.

EXPERIMENTAL

$[\text{}^{131}\text{I}]\text{IO}_3^-$

The isotope ^{131}I was obtained from Contor Isotope (Moscow, U.S.S.R.) in an isotonic solution of sodium chloride. After evaporation iodate was synthesized by adding 10^{-3} M sodium peroxodisulphate ($\text{Na}_2\text{S}_2\text{O}_8$) in a weakly acidic solution and heating for 10 min in a water-bath. Syntheses with chloramine-T in perchloric acid (pH 2–4) at room temperature were also successful.

The reaction yields were controlled by electromigration of $[\text{}^{131}\text{I}]\text{IO}_3^-$ in an aqueous perchlorate solution. Separation from $[\text{}^{131}\text{I}]\text{I}^-$ proceeds because the iodate ion moves significantly more slowly than the iodide ion.

The tests showed that the syntheses were complete. Amounts of $\leq 5\%$ of iodide were neglected in the iodate electromigration measurements.

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TABLE I

PROTOLYSIS CONSTANTS OF IODATE ION PUBLISHED UP TO 1976^{6,7}

Con = conductivity; sol = solubility; sp = spectroscopy; nmr = nuclear magnetic resonance; ram = Raman spectroscopy; var = other methods.

Method	T (K)	μ	pK_a	Year
con	298.1	Variable	0.73	1903
con	298.1	0	1.14	1923
con	298.1	0	0.77	1927
con	298.1	0	0.77	1933
sol	298.1	0	0.74	1934
sol	298.1	0	0.79	1939
sol	298.1	0	0.79	1941
sol	301.1	0	0.82	1941
sol	308.1	0	0.84	1941
sp	298.1	0	0.78	1944
nmr	301.1	0	0.74	1959
sol	Room temp.	1 (Li)ClO ₄	0.33	1959
con	298.1	0	0.85	1962
ram	303.1	0	0.74	1965
var	298.1	0	0.80	1967
sol	274.1	1 (Li)ClO ₄	0.22	1973
sol	288.1	1 (Li)ClO ₄	0.30	1973
sol	298.1	1 (Li)ClO ₄	0.31	1973
sol	274.1	1 (Li)ClO ₄	0.57 (² H ₂ O)	1973
sol	288.1	1 (Li)ClO ₄	0.60 (² H ₂ O)	1973
sol	298.1	1 (Li)ClO ₄	0.63 (² H ₂ O)	1973

Electrolytes

For investigations of the protolysis equilibrium, inert salt solutions of the type H(K)NO₃ and H(Na)ClO₄ were used. The overall ionic strength (μ) and temperature (T) of the solutions were constant ($\mu = 0.25$ and $T = 298.1(2)$ K). For measurements of the pH of the electrolytes glass and potassium chloride electrodes, calibrated with standard buffer solutions, were used. The experimental error in the pH measurements was *ca.* 0.03. Doubly distilled water and chemically pure reagents were used to prepare the electrolyte solutions.

Not more than 5 μ l of the [¹³¹I]IO₃⁻ stock solution with pH and ionic strength close to those of the background electrolyte solution were injected into the start position of the electromigration tube.

Electromigration method

Details of the construction and measurement principles of the electromigration apparatus developed in our laboratory have been published elsewhere^{8,9}. Migration velocities were measured in a glass tube (40 mm \times 3 mm I.D.) by means of an NaI(Tl) scintillation detector. The detector continuously scanned the tube during the experiment. At the same time a multi-channel analyser, operating in the multi-scale mode, recorded time and distance covered by the radioelement zone from the beginning of the experiment.

Continuous electrolyte exchange in vessels containing platinum electrodes guaranteed constancy of the pH in the electromigration tube. Connection of this tube with electrodes through Nuclepore filters prevented generation of liquid flows and distortion of the shape of the radioelement zone. For details and a schematic view of the electromigration cell, see ref. 10.

Ion mobilities were determined at constant voltage gradients of $\Delta E = 10.00(1)$ and $5.00(1)$ V cm⁻¹ in solutions of pH ≥ 1 and pH < 1 , respectively.

RESULTS AND DISCUSSION

To study the protolysis reaction



the dependence of the overall ion mobility, $\bar{\mu}_{\text{IO}_3^-}$, on the proton concentration must be measured. Fig. 1 illustrates the experimental results as the function $\bar{\mu}_{\text{IO}_3^-} = f(\text{pH})$.

No significant differences or trends in the $\bar{\mu}_{\text{IO}_3^-}$ data between the nitrate and perchlorate electrolyte systems were observed. This is clear because replacement of the anionic component of the inert electrolytes does not affect the protolysis equilibrium. This was also the case with background cations K⁺ and Na⁺, at least at the overall ionic strength applied.

Calculations of the stoichiometric protolysis constant start from the experimental pairs ($[\text{H}^+]$; $\bar{\mu}_{\text{IO}_3^-}$) and the general electromigration equation for reaction 1:

$$\bar{\mu}_{\text{IO}_3^-} = \mu_{\text{IO}_3^-}^0 \alpha_{\text{IO}_3^-} = \frac{\mu_{\text{IO}_3^-}^0 K_a}{K_a + [\text{H}^+]} \quad (2)$$

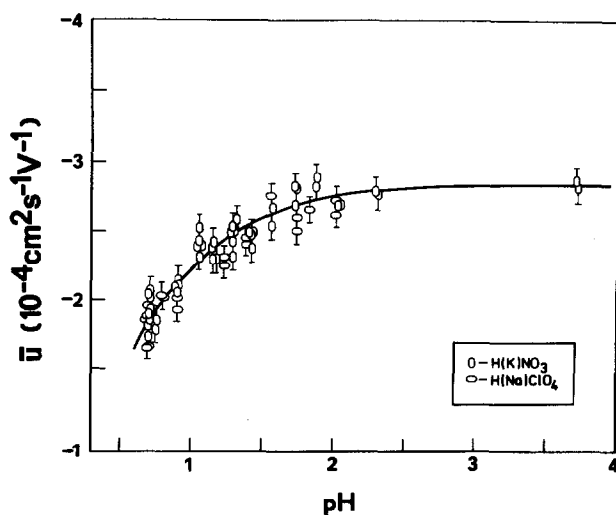


Fig. 1. Overall ion mobilities of [¹³¹I]IO₃⁻ versus pH of background electrolytes H(K)NO₃ and H(Na)ClO₄. $\mu = 0.25$; $T = 298.1(2)$ K.

where $\bar{u}_{\text{IO}_3^-}$ is the overall ion mobility of IO_3^- in the equilibrium reaction of interest, $\alpha_{\text{IO}_3^-}$ is the molar fraction of IO_3^- , $u_{\text{IO}_3^-}^0$ is the individual ion mobility of IO_3^- , valid at $\alpha_{\text{IO}_3^-} = 1$, and K_a is the stoichiometric protolysis constant.

Both the variables K_a and $u_{\text{IO}_3^-}^0$ in eqn. 2 were calculated by the least-squares fit of the experimental function $\bar{u}_{\text{IO}_3^-} = f([\text{H}^+])$ using the MINUIT program¹¹. The results are $u_{\text{IO}_3^-}^0 = -2.82 \pm 0.05 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ and $K_a = 0.37 \pm 0.01 \text{ mol l}^{-1}$ ($\text{p}K_a = 0.44 \pm 0.01$). The value of K_a calculated for $\mu = 0.25$ corresponds to the literature data for $\mu = 0$ and $\mu = 1$ and the weak dependence of the iodate protolysis constant on the overall ionic strength.

The results demonstrate the analytical capacity of the modified electromigration method for the investigation of protolysis equilibria of γ -radioactively labelled oxoanions. Similar demonstrations of the hydrolysis and complex formation of γ -radioactively labelled metal cations are summarized in refs. 12 and 13. It should be emphasized that by variation of the experimental electrolyte parameters (μ , T), thermodynamic protolysis data and information on the individual ion mobility behaviour can be obtained.

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