Mechanism and reaction rate of the Karl-Fischer titration reaction. Part IV. First and second order catalytic currents at a rotating disk electrode

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Short communication

MECHANISM AND REACTION RATE OF THE KARL-FISCHER
TITRATION REACTION

PART IV. FIRST AND SECOND ORDER CATALYTIC CURRENTS AT A
ROTATING DISK ELECTRODE

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The oxidation of the monomethyl sulfite ion by iodine and triiodide (which is the basic reaction in a Karl-Fischer titration) has been investigated with a potentiometric technique [1] and with the rotating ring-disk electrode [2] in Parts I and II, respectively. Both methods demand a rather high iodide concentration. In the potentiometric method, the potential of the indicator electrode must be only a function of the triiodide concentration and therefore the iodide concentration must remain constant. In the ring-disk electrode method, the current through the disk electrode must only be controlled by the galvanostat and may not be limited by diffusion phenomena.

No such demand exists for the measurement of limiting currents at a rotating disk electrode; on the contrary, it is necessary to have a small iodide concentration. As has been pointed out in Part I, the overall third order rate constant, k_3 , is a function of the iodide concentration:

$$k_3 = (k_{3,I_3^-} \cdot K_s c_{I^-} + k_{3,I_2}) / (1 + K_s c_{I^-}) \quad (1)$$

where k_{3,I_3^-} and k_{3,I_2} are the individual third order rate constants for triiodide and iodine, respectively, and K_s is the stability constant of the triiodide ion [3]:

$$K_s = c_{I_3^-} / c_{I^-} \cdot c_{I_2} = 2 \times 10^4 \text{ l mol}^{-1} \quad (2)$$

Because of the small iodide concentration used, the term $K_s c_{I^-}$ will be in the order of one and the simplification that led to eqn. (28) of Part I is not allowed. However, k_{3,I_2} is more than four orders of magnitude larger than k_{3,I_3^-} [the average values from (1) and (2) are: $8 \times 10^6 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ and $5 \times 10^2 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$, respectively], so that, as long as c_{I^-} is relatively small, the

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therm $k_{3,I_3^-} \cdot K_s c_{I^-}$ is negligible with respect to k_{3,I_2} and we may write:

$$k_3 \approx k_{3,I_2}/(1 + K_s c_{I^-}) \quad (3)$$

We expect therefore rather high values of the overall third order rate constant, which are virtually only due to the contribution of the rate constant of iodine.

The method for measuring the rate constant of the reaction of iodine with the methyl sulfite ion:

is that developed for catalytic currents. The theory for first order catalytic currents at a rotating disk-electrode by Levich [4] and Hale [5] shows, that a very good approximation of the exact solution for

$$q = i_k/i_d \quad (6)$$

(i.e. the ratio of the catalytic current in the presence of methyl sulfite and the diffusion current in the absence of it) is given by

$$q = \sqrt{\lambda}/\tanh \sqrt{\lambda} \quad (7)$$

with

$$\lambda = 2.60 (\nu/D)^{1/3} k_1/\omega \quad (8)$$

i.e. the dimensionless pseudo-first order rate constant used in Part II. The relative amount of methyl sulfite consumed near the electrode determines whether a pseudo-first order or a second order calculation must be applied. It can be shown [6] that this amount depends on the relative magnitude of the catalytic current, q , and the ratio iodide:methyl sulfite in the bulk of the solution:

$$c_{RSO_3^-}^0/c_{RSO_3^-}^\infty = 1 - p(q - 1) \quad (9)$$

where

$$p = 0.5 c_{I^-}^\infty/c_{RSO_3^-}^\infty \quad (10)$$

The coefficient 0.5 in eqn. (10) stems from the coefficient 2 in eqns. (4) and (5); the superscripts 0 and ∞ denote, respectively, the electrode surface and the bulk of the solution.

It is possible [6] to obtain a relation

$$q = f(\lambda, p) \quad (11)$$

by means of series expansion of the differential equations of the catalytic system. We prefer, however, the digital simulation technique as described by Feldberg [7]. The results of applying this technique are shown in Fig. 1.

For $p = 0$ there is an infinite excess of methyl sulfite and the catalytic reaction is first order. The results of the digital simulation for this case are equal to those obtained by Hale [5].

EXPERIMENTAL

The reagents used and the procedure applied in this investigation were grosso modo the same as those mentioned in the previous Parts. The disk electrode

Fig. 1. Dependence of q on λ and p , calculated with the method of digital simulation.

used was actually the disk of the ring-disk electrode no. 2 in Part II ($r_1 = 2.011$ mm); the ring was not connected. The electrode was controlled by a Tacussel PRT 30-01 potentiostat with a UAP 4 pulse unit that contained the potential control and the current measurement amplifiers. More details are given in ref. 6.

RESULTS AND DISCUSSION

The usual way to measure rate constants of homogeneous reactions by means of catalytic currents is to select such conditions, that a pseudo-first order regime is established. In the present case, this means that the concentration of water and sulfur dioxide must be much larger than the concentration of iodide. A relatively large water concentration causes no problem, as long as it becomes not too large (cf. Part II). A moderately large sulfur dioxide concentration, however, deforms the voltammograms [6], so that it becomes very difficult to obtain a useful limiting current plateau, especially at pH values larger than pK_a , where most of the sulfur dioxide is converted into the methyl sulfite ion [1]

$$K_a = c_{H^+} c_{CH_3SO_3^-} / c_{SO_2} = 10^{5.1} \quad (12)$$

Fig. 2. Dependence of the rate constant on the sulfur dioxide concentration. $c_{\text{I}^-}^{\infty} = 2 \times 10^{-4} \text{ M}$, $\omega = 25 \text{ rps}$. (a) $\text{pH} = 2.6$, $c_{\text{H}_2\text{O}} = 0.225 \text{ M}$; (b) $\text{pH} = 4.1$, $c_{\text{H}_2\text{O}} = 0.111 \text{ M}$; (c) $\text{pH} = 7.1$, $c_{\text{H}_2\text{O}} = 0.075 \text{ M}$.

At low pH values, however, a large excess of sulfur dioxide can be used (e.g. a fiftyfold excess at $\text{pH} = 2.6$), so that then first order measurements can be made.

The dependence of the reaction rate on the (formal) sulfur dioxide concentration and on the water concentration is shown in Figs. 2 and 3, respectively. Clearly, the reaction is first order, both in sulfur dioxide and in water. At high currents (high reaction rates), some passivation of the electrode occurs, so that the reaction rate and the reagent concentration are no longer proportional.

Fig. 3. Dependence of the rate constant on the water concentration. $c_{\text{I}^-}^{\infty} = 2 \times 10^{-4} \text{ M}$, $c_{\text{SO}_2}^{\infty} = 1 \times 10^{-4} \text{ M}$, $\omega = 25 \text{ rps}$. (a) $\text{pH} = 4.1$, (b) $\text{pH} = 7.2$.

Fig. 4. Dependence of the third order rate constant on the pH, at $c_{I^-}^\infty = 2 \times 10^{-4} M$.

The third order rate constant shows a similar dependence on the pH (Fig. 4) as in the previous parts, indicating that not sulfur dioxide but the methyl sulfite ion is the oxidizable species. The points in Fig. 4 are the mean values of several measurements with different rotation speeds and concentrations of water and sulfur dioxide. The average value of the rate constant is $(2.6 \pm 0.2) \times 10^6 l^2 mol^{-2} s^{-1}$, at a bulk concentration of iodide of $2 \times 10^{-4} M$. At the limiting current the iodide concentration varies from zero near the electrode to the bulk value at some distance from the electrode. It seems reasonable to estimate an average (effective) iodide concentration of approximately half the bulk concentration, and with this effective iodide concentration we calculate with eqn. (3) the third order rate constant for iodine:

$$k_{3,I_2} = 7.8 \times 10^6 l^2 mol^{-2} s^{-1}.$$

This value agrees fairly well with the values previously found (8.8×10^6 in Part I, 7.3×10^6 in Part II). It is not possible with the present method to measure any contribution to the reaction rate by triiodide. The only effect of the formation of triiodide is that some of the iodine is taken away. In the previous parts, triiodide was the predominant species, but, because of the large rate constant of iodine, the presence of even a small amount of this species had a marked effect on the overall rate constant, so that both the individual rate constants of iodine and triiodide could be determined.

We have tested the influence of pyridine on the reaction rate. With the pH fixed at a value of pH = 7, addition of pyridine (even to a concentration of 1 M, i.e. a fivethousandfold excess over iodide) does not, within experimental error, affect the reaction rate. This is in agreement with previous observations.

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