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MECHANISM AND REACTION RATE OF THE KARL FISCHER TITRATION REACTION

Part V. Analytical Implications

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SUMMARY

The Karl Fischer titration procedure for the determination of water has been studied. In view of the results of previous investigations, a methanolic sodium acetate—sulfur dioxide solution is recommended as solvent and an iodine solution in methanol as titrant. The advantages of this procedure over a conventional Karl Fischer titration are: a much more rapidly reacting reagent, the possibility of a visual end-point detection, a titrant of constant titre over a long period of time, and the absence of the disagreeable odour of pyridine.

The two-step mechanism proposed by Smith et al. [1] for the Karl Fischer titration reaction is, in spite of some severe criticism [2, 3], still generally accepted

where $\text{Py} = \text{C}_5\text{H}_5\text{N}$. It has been shown [4, 5] that pyridine plays no role in the mechanism, provided that the pH of the solution is kept constant. The oxidizable species in the reagent is neither sulfur dioxide, nor a pyridine—sulfur dioxide complex, but the monomethyl sulfite ion

It is therefore necessary to buffer the solution to be titrated to convert as much sulfur dioxide into methyl sulfite as possible. Another advantage of good buffering is that little of the yellow complex of sulfur dioxide and iodide [6] ($K_c \approx 1 \text{ l mol}^{-1}$) is formed

Thus, a visual end-point detection is possible, for this complex is the cause of the yellow color of spent reagent; the equipment for a biamperometric or a bipotentiometric end-point detection is not then required. The titration reaction is first order in methyl sulfite, in water, and in iodine, with a third-order rate constant, $k_{3,1} = 8 \times 10^6 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ (average of the values published [4–6] previously. Because of the great stability of the triiodide ion in methanol [7]

$$K_3 = c_{\text{I}_3^-} / c_{\text{I}_2} \cdot c_{\text{I}^-} = 2 \times 10^4 \text{ l mol}^{-1}, \quad (5)$$

generally most of the iodine will be converted into triiodide. The reaction is also first order in triiodide, but the rate constant for this species is much smaller than that for iodine: $k_{3,1,-} = 5 \times 10^2 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$. The effective rate constant for the reaction of both iodine and triiodide can be expressed as

$$k_3 = (k_{3,1} + k_{3,1,-} K_3 c_{\text{I}^-}) / (1 + K_3 c_{\text{I}^-}) \quad (6)$$

Thus the greater the iodide concentration, the greater the conversion of iodine into triiodide and the lower the effective rate constant k_3 .

THEORETICAL CONSIDERATIONS

It is customary with the Karl Fischer method for methanol to be used as solvent. Before the sample is added, the solvent is pre-titrated to a sensitive, but arbitrary end-point (e.g., in biamperometric end-point detection to a current greater than $10 \mu\text{A}$, lasting for at least 20 s when one drop of reagent is added). After addition of the sample, the solution is titrated to the same end-point.

This procedure introduces a systematic error: the volume at the end of the pre-titration differs from that at the end of the sample titration [8]. This error can be kept within acceptable limits by proper choice of the initial volume, concentration of the reagent and volume of the sample added. More important, however, is the difference in reaction rate. Usually, the reagent contains an approximately three-fold excess of sulfur dioxide over iodine, so that on addition of each drop of reagent the sulfur dioxide concentration in the titration vessel increases. At the end of the pre-titration, the sulfur dioxide concentration (assuming that the original solvent is reasonably dry) will be small; generally, this will not be so at the end of the sample titration. Since the detection of the end-point depends on the lifetime of a drop of reagent, and therefore on the reaction rate, this difference could cause serious errors. However, the iodide concentration will also increase during the titration so that, according to eqn. (6), the effective rate constant will decrease. These effects compensate each other to a large extent, so that in practice the systematic error is small. Nevertheless one of the drawbacks of the Karl Fischer reagent is the slow reaction rate and, therefore, the tedious titration and the dragging end-point. The remedy is to increase the reaction rate by increasing the sulfur dioxide concentration, or better, by

increasing the pH of the solution. Normally, pyridine is added as buffer with each drop of reagent (usually, the reagent contains a seven-fold excess of pyridine over iodine). Pyridine and sulfur dioxide have approximately the same acidity constant [4] in methanol

$$K_{a,Py} = c_{Py} c_{H^+}/c_{PyH^+} = 10^{-5.6} \quad (7)$$

$$K_{a,SO_2} = c_{RSO_3^-} c_{H^+}/c_{SO_2} = 10^{-6.0} \quad (8)$$

(these values depend somewhat on the ionic strength of the solution), so that a reasonable estimation of the methyl sulfite concentration is

$$c_{RSO_3^-} \approx 0.5 f_{SO_2} \quad (9)$$

where f_{SO_2} is the formal (analytical) concentration of sulfur dioxide. Unless very large amounts of water are titrated, the sulfur dioxide concentration will remain relatively low. It is therefore proposed that a methanolic solution of sulfur dioxide (ca. 0.5 M) and sodium acetate (ca. 1 M) is used as solvent and a solution of iodine in methanol as titrant. Because the dissociation constant of acetic acid in methanol is very small [9]

$$K_{a,HAc} = c_{Ac^-} c_{H^+}/c_{HAc} = 10^{-9.7}, \quad (10)$$

the sodium acetate will convert virtually all of the sulfur dioxide into methyl sulfite

and the solution in effect contains a solution (0.5 M + 0.5 M) of acetate—acetic acid buffer.

The advantages of this procedure are: (1) the good buffer action and the large methyl sulfite concentration give a high reaction rate; (2) the absence of sulfur dioxide prevents the formation of the yellow SO_2I^- complex and makes a visual end-point possible; (3) the absence of pyridine makes the reagent more agreeable to use; (4) the iodine titre remains constant.

The only disadvantages are: (1) two separate solutions are necessary; (2) the maximum amount of water that can be titrated depends on the amount of buffer present, i.e. on the buffering capacity of the solution. The appearance of a yellow colour before the end-point is a good indication that the buffer capacity is not adequate. If, on further addition of iodine, the intensity of the colour does not increase, formation of the SO_2I^- complex is indicated.

Some titration curves, whereby the lifetime of a drop of reagent is calculated as a function of the total amount of reagent added, have been constructed. By the lifetime of a drop is understood the time needed for the iodine therein to be consumed and a certain detection limit to be reached (expressed in terms of concentration in the titration vessel, see below). For the sake of simplicity, some approximations are made: (1) the mixing time of the drop with the sample solution is neglected; (2) the overall third-order rate constant does not change during the drop life; (3) the methyl sulfite concentration of the solution is constant during the drop life.

The first approximation is required as it would be very difficult — if not impossible — to calculate the flow patterns of the mixing of the drop, the concentration profiles in the solution and the influence of these factors on the drop life. In practice, the mixing time is ca. 1 s. The second approximation implies that variation of the iodide concentration during a drop life is small. For the first few drops this condition is not fulfilled but, from an analytical point of view, these first few drops are not important. Figure 1 shows the dependence of the overall third-order rate constant, k_3 , on the iodide concentration (eqn. 6). When the iodide concentration is very small, the reaction rate constant decreases very rapidly with increasing iodide concentration; for the relatively large iodide concentration usually found at the end of a titration, the decrease in rate constant is much smaller and the second approximation is justified.

The third approximation makes it possible to calculate the drop life with pseudo-second order kinetics. If the initial sulfur dioxide concentration (at the beginning of the customary titration) is zero, some error is incurred; again, this is not pertinent analytically. The calculation is as follows: for the n th drop of reagent added, the initial concentrations of water and methyl sulfite, $c_{H_2O}^{n,0}$ and $c_{R_{SO_3}^-}^{n,0}$, are calculated. Then, the initial concentrations of iodine, triiodide and iodide are calculated. From eqn. 6, the third-order rate constant for the n th drop, k_3^n , is found, and multiplication by $c_{R_{SO_3}^-}^{n,0}$ gives the second-order rate constant, k_2^n : this is considered to remain constant during the lifetime of the n th drop τ_n .

Second-order kinetics give:

$$\tau_n = \frac{1}{k_2^n (c_{O_x}^{n,0} - c_{H_2O}^{n,0})} \ln \frac{c_{H_2O}^{n,0} \cdot c_{O_x}^{n,\tau}}{c_{O_x}^{n,0} (c_{H_2O}^{n,0} - c_{O_x}^{n,0} + c_{O_x}^{n,\tau})} \quad (12)$$

where $c_{O_x}^{n,0} = c_{I_2}^{n,0} + c_{I_3}^{n,0}$ and $c_{O_x}^{n,\tau}$ is the detection limit of iodine and triiodide at the end of the life of the n th drop.

Fig. 1. Dependence of the effective third-order rate constant on the iodide concentration.

In Fig. 2, some titration curves are shown for a pre-titration with a sample titration. The following values for the various quantities have been used in the calculation. The initial volume and the volume of a drop of reagent are taken as 10 ml and 0.01 ml, respectively. Before addition of the sample, the water concentration in the titration vessel is 1 mM, and the sample increases the water concentration in the vessel by a further 10 mM. The pre-titration, therefore, demands 10 drops of reagent (0.1 ml) and the sample consumes 100 drops of reagent (1 ml). The detection limit is estimated as 0.03 mM ($I_2 + I_3^-$). Figure 2(a) shows the titration curve for the customary reagent ($\text{pH} = \text{p}K_a$; threefold excess of sulfur dioxide over iodine in the reagent). Figure 2(b) shows the titration curve for the same reagent, but with increased pH. Figure 2(c) shows the titration curve for the modified procedure in which the initial solution contains 0.5 M methyl sulfite and sulfur dioxide is not added during the titration. For the sake of clarity, the titration curves are drawn as solid lines rather than as discrete points for each drop. The amount of reagent used for the sample titration equals the distance between corresponding points in the pre-titration curve and the sample titration curve. If the end-point corresponds to a drop life of 20 s, this distance corresponds in Fig. 2(a) to 0.95 ml of reagent (i.e. a systematic error of -5%). At 30 s, the systematic error is -2.5% , at the expense of a more tedious titration. For the modified reagent, however, this error is negligible at 2 s or more.

Figure 3 shows the values of the second-order rate constant for the different cases in Fig. 2. Except for the first few drops, the decrease in the rate constant as a result of the increasing concentration of iodide is compensated largely by the increase in sulfur dioxide concentration (Fig. 3a and b). For the modified procedure (Fig. 3c), there is no such compensation and the variation of the second-order rate constant is much larger. However, this rate constant is, even at the end of the titration, so high that all drops are very rapidly consumed and the variation in the second-order rate constant has no effect.

Because of the approximations mentioned above, the results of the calculations are indicative rather than absolute. They show, however, the shortcomings of the customary reagent and the improvements obtained by increasing the pH and the methyl sulfite concentration. For the measurement of rate constants, the calculations are, of course, not suitable. The better-defined conditions and more accurate measuring techniques of previous parts of this series are much more suitable for this purpose.

EXPERIMENTAL

Reagents and procedure

The methanol used to prepare the titration solutions (Baker, A.R.) was dried by distillation after refluxing with magnesium. Sodium iodide (Baker A.R.) and sodium acetate (Merck, A.R., anhydrous) were dried at 150°C for

at least 24 h. Iodine (Baker, A.R.) and sulfur dioxide (Baker—Matheson, anhydrous gas) were used without further purification. Both single and double Karl Fischer reagents (Merck and Baker) were used. The titre of the reagents was determined with water, injected into the titration vessel through a rubber septum with a 10- μ l Hamilton microsyringe.

Apparatus

The customary Karl Fischer reagent and methanolic iodine solution were inserted into the titration vessel from a 5-ml electronic burette (Metrohm Dosimat E 535/E 552-5B) with a resolution of 0.001 ml. The original Teflon tip was replaced by a very fine glass capillary that just reached the solution surface. The methanol and the methanolic solution of sulfur dioxide and sodium acetate were added from a 20-ml burette (Metrohm Dosimat E 415/E 552-20B) with a resolution of 0.01 ml. The burettes were fitted with Teflon cocks. The supply vessels of the burettes could be opened to the atmosphere via a drying tube, filled with silica gel or phosphorus pentoxide; a cock between the supply vessels and the drying tubes was opened occasionally for a few seconds to equalize the pressure in the supply vessels, thus preventing the drying material from interacting with the methanol vapours.

Bipotentiometric and biamperometric end-points were detected with a pair of platinum wire electrodes (ca. 5 mm long, 5 mm apart) and a laboratory-made potentiostat/galvanostat. Some titrations were performed with a Metrohm autotitrator E 526-1 to which some minor modifications were made. The coulometric experiments were performed as described [4] with a cell of reduced size (main compartment, 9-ml capacity).

Fig. 2. Calculated titration curves. (a) Customary Karl Fischer reagent, (b) effect on (a) of increased pH, (c) modified procedure (see text).

Fig. 3. Second-order rate constants for the titration of Fig. 2.

RESULTS AND DISCUSSION

For a customary Karl Fischer reagent, electroanalytical end-point detection is normally used. Figure 4 shows bipotentiometric detection curves (E vs. total c_{I_2} , i.e. inclusive triiodide) for various electrode currents. Bipotentiometric detection is well-suited for triggering purposes because of the steep drop in potential difference. A potential-controlled timing device was started when the potential difference fell below 100 mV and was stopped when the difference exceeded 150 mV, thus indicating the lifetime of a drop of reagent. The hysteresis of 50 mV made the timing device insensitive to small fluctuations in the potential difference.

Figure 5 shows biamperometric detection curves (i vs. total c_{I_2}) for various potential differences between the indicator electrodes. The indication is approximately proportional to the total concentration of iodine (inclusive triiodide) and much more dependent on factors such as the rotation speed of the stirring magnet and concentration gradients in the titration vessel. The fluctuations in the indication are much larger, so that an automatic timing device cannot easily be used. Bipotentiometric end-point detection was therefore used. The electrode current was usually set at $2 \mu A$, corresponding to a detection limit of about 3×10^{-5} M. The bipotentiometric detection mode is acceptable in modern analytical practice; many pH meters have a Karl Fischer polarization current source.

For the modified procedure, a methanolic solution of sulfur dioxide (0.5 M) and sodium acetate (1 M) was used as solvent; the titration was made with either a customary Karl Fischer reagent or with a solution of iodine in methanol (0.1 M). Both titration reagents are equally satisfactory but the iodine solution is preferred; the titre of the customary Karl Fischer reagent decreases from ca. 0.3 M to 0.1 M over a period of a few months, but the effective titre of a methanolic iodine solution decreases by only 3% over a period of five months, probably through penetration of water into the supply vessel). The effective titre of the iodine solution is the difference between the analytical iodine concentration and the water concentration in that solution; in practice it differed by ca. 5% from the amount of iodine dissolved in the methanol.

Both bipotentiometric and visual end-points are possible; the latter is somewhat more sensitive (about 1×10^{-5} M).

The use of sodium acetate instead of pyridine has been reported previously [10]. A Karl Fischer reagent with the pyridine replaced by sodium acetate is not very stable and it was recommended that the reagent be stabilized by adding iodide. This, however, lowers the reaction rate; the stabilization and the lowering of the reaction rate can be attributed to the same effect. It has been suggested [4] that an iodine—methyl sulfite complex might be an intermediate in the Karl Fischer reaction

The actual Karl Fischer reaction then involves the hydrolysis of this complex

The complex is also thought to react with methanol, but the rate of solvolysis is much smaller

Dimethyl sulfate is very toxic; a Karl Fischer reagent should therefore be handled with care. The introduction of a large amount of iodide will convert most of the iodine into triiodide. In this respect, the use of separate solutions for sulfur dioxide and iodine contributes to safety in the laboratory; the use of separate solutions has been suggested previously [11, 12]. In Fig. 6, the experimental titration curves are shown for (a) a customary Karl Fischer titration and (b) the modified titration. There is a fair similarity between these curves and the theoretical predictions. For ca 1 y, a customary and a modified reagent have been compared in use. The water content of many non-aqueous solvents used in the laboratory has been measured, e.g. the methanolic solutions used previously [4-6] and non-aqueous solutions for electrochemical experiments, e.g. dimethyl sulfoxide, dimethylformamide, propylene carbonate, etc. The variations in the determinations by the two methods are of the same order of magnitude as the variation within one method (1-2%). The modified procedure is much faster. It is sufficient to check the titre of the iodine solution weekly.

The applicability of the modified reagent to coulometric determinations has been tested. The cell was filled with the sulfur dioxide - sodium acetate solution and iodide (0.1 M). The solution was coulometrically pre-titrated (if the glassware is not very dry, it is faster to pre-titrate the solution with

Fig. 4. Bipotentiometric detection curves for different electrode currents; $c_{\text{I}^-} = 0.1 \text{ M}$ in methanol.

Fig. 5. Biamperometric detection curves for different potential differences $c_{\text{I}^-} = 0.1 \text{ M}$ in methanol.

Fig. 6. Experimental titration curves. (a) Titration of 4 μ l of water with 0.25 M Karl Fischer reagent; (b) titration of 2 μ l of water with 0.11 M iodine solution in methanol; $c_{\text{NaAc}} = 1 \text{ M}$, $c_{\text{SO}_2} = 0.5 \text{ M}$, drop volume = 0.01 ml.

an iodine solution) and small amounts of water were injected with a Hamilton 1- μ l microsyringe through a rubber septum. For the coulometric determinations, the current source for the generation of iodine, set at 25 mA, was controlled by the Metrohm autotitrator. The switching potential was set at 100 mV. The autotitrator was slightly modified; e.g. a polarization current source (2 μ A) for the platinum wire detector electrodes was added. The overall current efficiency was excellent ($99.1 \pm 0.1\%$ inclusive of the tolerances in the electronic equipment and the microsyringe) when the method was tested over the range 1–12 μ g of water.

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