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SHORT COMMUNICATION

Some remarks on mechanism and kinetics of the coulometric variant of the Karl-Fischer titration reaction

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In many non-aqueous solvents water can be determined by the well-known Karl-Fischer titration method. Often, the coulometric variant is applied, among others, because of its suitability for automation.

Contrary to the classical titration reaction:  
\[ \text{C}_6\text{H}_5\text{N}_2\text{I}_2 + \text{C}_6\text{H}_5\text{N}_2\text{SO}_2 + \text{C}_6\text{H}_5\text{N} + \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 2\text{C}_6\text{H}_5\text{N}_2\text{HI} + \]  
\[ + \text{C}_6\text{H}_5\text{NH}_2\text{SO}_3\text{CH}_3, \]

in the coulometric case iodine is generated at a platinum anode from an iodide solution (e.g. a spent Karl-Fischer solution) at the moment necessary, so that, moreover, no titre problems can arise.

Both the classical titration reaction and the coulometric variant are known to proceed rather slowly. Therefore, we started research to elucidate some aspects of the mechanism and kinetics of this variant, making use of a rotating ring–disk electrode for detecting the relevant reaction intermediates.

In first instance, the oxidation of iodide to iodine was studied in media as encountered under Karl-Fischer conditions.

Experimental

The rotating ring–disk electrode, as introduced by Frumkin et al., can be considered as a continuous flow system, in which the disk is the upstream generator (anode, at which iodine is formed) and the ring the downstream detector (generated iodine passes the ring and is reduced there).

Apparatus. Use was made of a platinum ring–disk electrode \((r_1 = 2.017 \text{ mm, } r_2 = 2.147, r_3 = 3.028 \text{ mm, } N_o (\exp.) = 0.478; r_1, r_2, r_3 \) are the radius of the disk, the inner and outer radius of the ring, respectively, \(N_o\) being the collection coefficient) with servomotor and tachogenerator for controlling the rotation speed. Recordings were made with a dual potentiostat (Bipad-2) with function generator (GSTP-3) made by Tacussel (France) and a dual pen recorder (Hewlett-Packard 7046A).

The cell has, besides the sample compartment, separate compartments for the auxiliary and the reference electrode; the connections with the main compart-
ment (150 ml) were made by a glass frit for the auxiliary electrode compartment (15 ml) and by a Luggin capillary for the reference electrode compartment (10 ml). The auxiliary electrode is a platinum wire, the reference electrode a saturated calomel electrode in methanol.

Reagents. Unless otherwise stated, all experiments have been performed in methanol (Baker, A.R.), distilled after drying by refluxing with magnesium (Merck). It is very difficult to get down the water content below $10^{-3}$ M in the cell. Supporting electrolyte: lithium nitrate dried at ca. 230°C for at least 24 h (Baker, A.R., 0.5 M in methanol). Further: anhydrous sulphur dioxide (Baker), pyridine (Baker, A.R.), sulphur dioxide in pyridine (Merck), sodium iodide (Baker, A.R.) and Karl-Fischer reagent (Merck).

Procedure. First, the main compartment of the cell was filled up to 130 ml with methanol, supporting electrolyte and, according to the experiment to be performed with one or more of the following constituents: sulphur dioxide, water, pyridine, and sodium iodide. Oxygen was removed by bubbling through purified nitrogen, previously dried over phosphorous pentoxide; during each experiment nitrogen was passed over the solution. Via a septum, 10 ml of the solution was taken from the cell and titrated by the classical Karl-Fischer method to determine the actual concentration of water in the cell. The electrode was rotated at 25 r.p.s. The potential of the disk electrode was scanned from 0 to +1.0 V vs. SCE (methanol) at a rate of 5 mV s⁻¹, whilst the potential of the ring electrode was fixed at 0 V vs. SCE (methanol). Sometimes use was made of the galvanostatic mode of the potentiostat.

Results and discussion
In many solvents iodide can be oxidized in two steps:\n
\[
2 \text{I}^- \rightleftharpoons \text{I}_2 + 2e^- \quad (1a)
\]
with
\[
\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^- \quad (1b)
\]
and
\[
2 \text{I}_3^- \rightleftharpoons 3 \text{I}_2 + 2e^- \quad (2)
\]
It depends on the stability of the triiodide ion in the solvent as well as on the concentration of the iodide whether two distinguishable steps are found. In a number of solvents the respective half wave potentials can differ up to 300 mV.

In our experiments iodide is oxidized at the disk, while the iodine or triiodide formed is partly reduced at the ring electrode. If only iodide and some water are present in solution, the ratio of the ring current to the disk current ($i_R/i_D$) is equal to $-N_0$, this value being independent of the speed of rotation and the concentration of iodide.

Sulphur dioxide itself, in the potential range studied, is scarcely anodically oxidizable in methanol. However, on addition of a relatively large excess of sulphur dioxide to a methanolic solution of iodide (e.g. 30 times the iodide concentration), the disk current increases and the ring current decreases (Fig. 1), indicating that chemical oxidation of sulphur dioxide by generated iodine or triiodide takes place. If, moreover, pyridine is added, the disk current increases considerably and the ring current becomes very small (curve 3). The limiting current
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Fig. 1. Ring current ($i_R$) and disk current ($i_D$) for the following systems: (1) 500 mM LiNO$_3$ + 12 mM H$_2$O in methanol with 3 mM NaI; (2) addition of 93 mM SO$_2$; (3) addition of 290 mM pyridine to the previous system; (4) addition of 86 mM H$_2$O to the previous system.

in this curve is caused by water, since addition of water enhances the current (curve 4).

It is therefore of interest to investigate to what extent the respective constituents of the Karl-Fischer reagent can influence the reaction. So, we examined different series of solutions in which each time one of the constituents was limiting the anodic current. The effect of increasing amounts of water in a solution of 3 mM I$^-$, 100 mM SO$_2$, 300 mM Pyr and 500 mM LiNO$_3$ in methanol is shown in Fig. 2. Figure 3 shows the influence of SO$_2$ in a solution of 3 mM I$^-$, 103 mM Pyr, 14 mM H$_2$O and 500 mM LiNO$_3$ in methanol. The increase of the disk current is proportional to the sulphur dioxide concentration.

From Fig. 4 one can see that further addition of pyridine (in a methanolic solution of 3 mM I$^-$, 100 mM SO$_2$, 14 mM H$_2$O and 500 mM LiNO$_3$) has no influence as soon as its concentration equals the sulphur dioxide concentration. This observation, combined with the fact that sulphur dioxide forms an adduct with pyridine, C$_5$H$_5$N.SO$_2$, leads to the conclusion that not sulphur dioxide itself but this adduct is essential in the functioning of the Karl-Fischer reagent.

Figure 5 shows that the disk current is proportional to the iodide concentration in a solution of 13 mM H$_2$O, 100 mM SO$_2$, 300 mM Pyr and 500 mM LiNO$_3$. The increase of the disk current is 11.8 $\mu$A cm$^{-2}$ per micromolar of iodide, whereas the diffusion current of iodide alone is 0.74 $\mu$A cm$^{-2}$ per micromolar (at 25 r.p.s.). This suggests a catalytic action of the iodide adsorbed on the disk surface during the oxidation of the sulphur dioxide–pyridine adduct. So we propose a cyclic mechanism:

\[ \rightarrow 2 \text{I}^- (\text{ads}) - 2e^- \rightarrow 2 \text{I} (\text{ads}) \rightarrow \text{I}_2 (\text{ads}) \]

\[ 2 \text{I} (\text{ads}) \text{ or I}_2 (\text{ads}) + \text{Pyr}.\text{SO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{I}^- (\text{ads}) + \text{Pyr}.\text{SO}_3 + 2 \text{H}^+ \]
Fig. 2. Effect of addition of water. 500 mM LiNO₃ + 3 mM NaI + 300 mM Pyr + 100 mM SO₂ in methanol. [H₂O] = (1) 6, (2) 10, (3) 14, (4) 18, (5) 22 and (6) 30 mM.

Fig. 3. Effect of addition of sulphur dioxide. 500 mM LiNO₃ + 14 mM H₂O + 103 mM Pyr + 3 mM NaI in methanol. [SO₂] = (1) 0, (2) 5, (3) 10, (4) 15 and (5) 20 mM.

Fig. 4. Effect of addition of pyridine. 500 mM LiNO₃ + 14 mM H₂O + 100 mM SO₂ + 300 mM NaI in methanol. [Pyr] = (1) 0, (2) 30, (3) 60, (4) 90, (5) 120, (6) 150 and (7) 300 mM.

Fig. 5. Effect of addition of iodide. 500 mM LiNO₃ + 13 mM H₂O + 100 mM SO₂ + 300 mM Pyr in methanol. [I⁻] = (1) 0, (2) 15.9, (3) 31.7, (4) 47.6, (5) 63.5, (6) 79.4 and (7) 95.2 μM.
whereby I\(^-\) (ads) as well as I\(^3-\) may be complexed by pyridine. In this case, iodide is present near the electrode and does not have to be transported from the bulk of the solution. It therefore is not subject to limitation by diffusion. Little iodine is present outside the reaction film adhering the disk, so it is clear that the ring current (depending on the concentration of iodine or triiodide in solution) is very small.

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