Coulometric determination of organic compounds. III.
Determination of some phenoxazones by titanometric coulometry

V. STUŽKA and V. ŠTEFANIDESOVÁ

Department of Analytical and Organic Chemistry, Faculty of Natural Sciences,
*Palacký University, 771 46 Olomouc*

Conditions have been found for the determination of some phenoxazones by titanometric coulometry using platinum electrode to generate Ti(III) ions, while the point of equivalency was recorded potentiometrically. It has been found, that correct and accurate results can be obtained when the amount of ethanol in the coulometric vessel is within 2—7 ml and the amount of the substance determined is 0.2—0,6 mg in 50—100 ml. Acetone was found a suitable solvent in the determination of 9-diethylaminobenzo[a]phenoxaz-5-one.

В работе были найдены условия для кулонометрическо-титанометрического определения различных феноксазонов при постоянном токе и использовании блестящего платинового электрода для генерации ионов Ti(III) и при потенциометрическом определении точки эквиваленции. Было найдено, что результаты правильные и точные, если в кулонометрической ячейке по крайней мере 2 мл этанола и не больше чем 7 мл этанола для определения 0,2–0,6 мг веществ в 50–100 мл. Для определения 9-диэтиламинобензо[a]феноксаз-5-она был найден ацетон удобным растворителем.

We have previously found conditions for the determination of quinones [1] and azines [2] by titanometric coulometry. The objective of the present work was the determination of phenoxaz-3-one (*I*), benzo[a]phenoxaz-5-one (*II*), benzo[a]phenoxaz-9-one (*III*), and 9-diethylaminobenzo[a]phenoxaz-5-one (*IV*) (Scheme 1) by constant-current coulometry. The obtained results are presented in Table 1.

The substances under investigation are poorly soluble in water and better soluble in ethanol or acetone. It was found [2] when isorosindone and its derivatives were studied by titanometric coulometry that the presence of more than 10 ml of ethanol in the electrolytical vessel interferes with the determination. Therefore, prior to the determination of phenoxazones we first examined the effect of ethanol upon the analysis.

366

I   II, IV   III
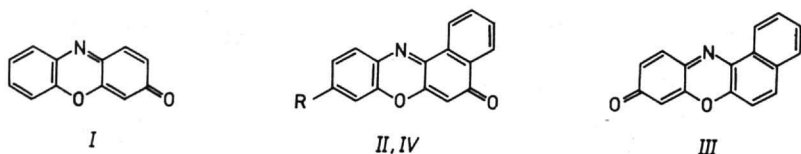
Scheme 1

II R = H
IV R = N(C₂H₅)₂

The determination of *I* was carried out in the presence of different total amount of ethanol in the coulometric vessel while the concentration of the substance was kept approximately constant (Table 1, No. *1—5*). It can be seen that most of the time the relative error is positive, only in the presence of 10 ml of ethanol a small negative relative error was observed. When 3—10 ml of ethanol is present in the solution *I* can be determined with a relative error of 0.6%. The results obtained by the method described herein are correct and accurate, as can be seen from the calculated values of the *t* criterion and a comparison with the theoretical values for

Table 1

Results of the determination of phenoxazones by titanometric coulometry

No.	Compound	Theoretical mg	Found[a] mg	s	e %	Notes
1	I	0,406	0,413	0,0056	+ 1.5	2 ml EtOH
2	I	0.415	0.417	0,0027	+ 0.4	5 ml EtOH
3	I	0.388	0.390	0.0042	+ 0,5	5 ml EtOH
4	I	0.462	0.459	0.0083	0.0083	7 ml Et+ 0.6
5	I	0.418	0.417	0.0079	− 0.2	10 ml EtOH
6	II	0.130	0.137	0.0010	+ 5.3	5 ml EtOH
7	II	0.184	0.186	0.028	+ 1.0	5 ml EtOH
8	ml EtOH	243	0.211	0.0013	− 13.1	10 ml EtOH
9	II	0.246	0.248	0.0016	+ 0.8	2 ml EtOH
10	II	0.364	0.362	0.0010	− 1.0	5 ml EtOH
11	II	0.720	0.744	0.0025	+ 3.3	10 ml EtOH
12	II	0.364	0.361	0.0030	− 0.8	5 ml EtOH, PE
13	II	0.204	0.201	0.0026	− 2.0	1 ml EtOH, PE
14	II	0.408	0.408	0.0027	0.0	2 ml EtOH, PE
15	II	0.408	0.411	0.0017	+ 0.7	2 ml EtOH, DR
16	III	0.404	0.404	0.0070	− 0.7	5 ml EtOH
17	IV	0.440	0.444	0,0047	+ 0.9	2 ml Me₂CO

a) Mean value of five or six measurements; *s* – deviation; *e* – relative error; PE — titration up to the point of equivalency; DR — derivation recording of the titration.

367

95% probability, and by comparison of the theoretical and found values, respectively. We have found later that I as well as its reduced form are better soluble in ethanol than are the other substances under investigation, which facilitates the determination with a small relative error even in the presence of only 2 ml of ethanol.

During the determination of II we investigated the effect of the amount of the analyzed substance in the solution upon the correctness of the analysis. A series of ten solutions containing 0.024—0.720 mg of II were analyzed. The results obtained with the smallest amounts showed high positive error and even with 0.130 mg of II the relative error was +5.3 % (Table 1, No. 6). With 0.184 mg the relative error decreased to +1.0% and the determination complies with the Student t criterion of the correctness. The next two determinations differed from each other by the total volume of ethanol (Table 1, No. 8, 9). The determination was incorrect when 10 ml of ethanol was present; with 2 ml of ethanol the relative error was satisfactory and the determination of II complies with the t criterion. Satisfactory results were also obtained with larger amounts of II when the total amount of ethanol was 5 ml, but with 0.700—0.900 mg of II in 10 ml of ethanol high positive error was observed (Table 1).

The method described permits to determine II by constant-current titration with a relative error not exceeding 1% when the total volume of ethanol is 5.0 ml and the amount of the substance is 0.200—0.500 mg. The determination of II was carried out under the found suitable conditions and the solution was titrated to the point of equivalency (Table 1, No. 10). The potential in the point of equivalency for a sample of 0.364 mg in 5 ml of ethanol was determined. The determination was first conducted in one electrolyte. The first two titration curves were identical, but those found in further experiments were considerably deformed and phenoxazone gradually precipitated. Even when the determination of small amounts of II was carried out in this manner the results were largely erroneous. Under suitable conditions it was possible to perform only two titrations to the point of equivalency.

The determination of II to the potential of the point of equivalency was performed also with solution B (see Experimental). The same results were obtained as with solution A (Table 1, No. 13, 14). Compound II was determined also after the recorder EZ 2 was connected for the derivation recording of the potentiometric curve. Under these conditions the found relative error was +0.7% (Table 1, No. 15).

It was found in the determination of III that the substance can be determined with the relative error not exceeding 1% applying potentiometrical recording of the titration curve when each determination is done in fresh electrolyte.

Acetone has been found a suitable solvent for the determination of IV. Well reproducible results with a relative error up to +0.9%, complying with the Student t criterion were obtained.

Experimental

Compounds under investigation were prepared as described [3—6]. Their purity was checked by melting points (Kofler hot stage), elemental analyses (Perkin—Elmer Elemental Analyzer, Model 240) and thin-layer chromatography (Silica gel CH containing 10% gypsum, Spolana, Neratovice) using benzene—ethanol 4 : 1 as the mobile phase.

Instruments

A solid-state instrument set up according to [7, 8], as described in [1] was used as the source of the stabilized current which was measured with the accuracy of 0.2 mA using ML 20 instrument (Metra, Blansko).

An H-shaped electrolytical vessel was used. The volume of the cathode and the anode portions, separated with a fine sintered-glass filter $S3$, was 110 and 28 ml, respectively. The bore in the PVC lid of the cathodic space served as the holder of the electrodes. A platinum plate (0.7×0.5 cm) served as the generation electrode, the auxiliary electrode (0.4×0.1 cm) being made of the same material. The point of equivalency was determined potentiometrically. The indication electrode was made of a platinum plate (0.3×0.8 cm); saturated calomel electrode (K-401, Radiometer, Copenhagen) served as the reference electrode. The indication system comprised a $1 : 10$ voltage shunt and a compensating recorder EZ 4 which, at a sensitivity $5 \times$ and range 500 µV, was set to a chart speed of 20 mm/s. To record the derivation curves an EZ 2 recorder was used; the polarography filter was disconnected leaving only the derivation circuit in function. During these experiments the recorder was set at a chart speed of 20 mm/s, sensitivity $1 \times$ (range 100 µV). The electrolyte was stirred magnetically with a plastic coated stirring bar. Argon, the purity of which was found satisfactory by means of mass spectrometry, was used as the inert gas. The correct function of the apparatus was checked by the determination of arsenic (in arsenic(III) oxide) with bromine, generated coulometrically from potassium bromide in the presence of sulfuric acid. During these experiments the point of equivalency was indicated potentiometrically, while the whole curve was recorded. The results of the two consecutive determinations complied with the Student t test.

Solutions

The solutions were prepared using ethanol (middle fraction) purified by distillation. Air was bubbled for 3 h at 30°C through ethanol acidified with a few drops of concentrated hydrochloric acid prior to distillation. The purity of ethanol was checked by gas chromatography. Solutions of IV were prepared using the middle fraction of redistilled, reagent grade acetone.

Titanium(III) chloride was prepared by electroreduction of solutions of titanium(IV) chloride.

For preparation of solution A an oxidized, originally $\sim 15\%$ reagent grade solution of titanium(III) chloride (C. Erba, Milan) was used.

Solution B was prepared from reagent grade titanium(IV) chloride (International

Enzymes Limited, Windsor, Berkshire, England) in the following manner [9—11]: Distilled water was carefully added with stirring to titanium tetrachloride solution (200 ml). Vigorous hydrolysis occurred, the material precipitated but further addition of water caused dissolution. The final volume was adjusted to 500 ml. The obtained solution (~3.6 M) is stable over a period of six months. It was diluted ten times before use. Its pH is ~0.6 and it begins to hydrolyze 12—24 h after preparation. The concentration of both solutions was determined gravimetrically and it was proved that Fe(III) ions were not present.

Working procedure

A mixture of 2.14 M hydrochloric acid (40 ml) and 0.4 or 0.36 M titanium(IV) chloride (10 ml) was placed into the electrolytical vessel. The anodic portion was filled with 2.14 M hydrochloric acid. Inert gas was bubbled through the electrolyte (at least for 10 min) and the analyzed, ethanolic or acetone solution (through which argon was passed before pipetting) was added, and the generation current and the recorder were turned on. When the recording of the whole potentiometeric curve was complete the electrolytical vessel was emptied and, as well as the electrodes, rinsed with chromiumsulfuric acid and water. After five or six measurements the electrodes were cleaned by burning. During some measurements also the derivation curve was recorded, or the titration was run up to the point of equivalency.

The potentiometric curves were used for the determination of the point of equivalency (graphically, according to Hahn and Weiler [12]) and the time needed to reach it. The amount of the analyzed substance was calculated according to Faraday's law. When the titrations were run up to the point of equivalency the time needed to reach it was measured by means of a stop-watch which was turned on simultaneously with the generation current. The accuracy of the measurement depended upon the stabilization of the network frequency.

The thus obtained data served for the calculation of the mean value of five or six measurements and the deviation s. The calculated value of the Student t criterion for 95% probability ($\alpha = 0.05$) was compared with the tabulated value and the relative error e [13] (Table 1) was calculated.

References

1. Stužka, V., Lukáš, I., and Jílek, J. A., *Acta Univ. Palacki. Olomuc., Fac. Rerum Natur.* **49**, 93 (1976).
2. Stužka, V. and Císař, B., *Acta Univ. Palacki. Olomuc., Fac. Rerum Natur.*, in press.
3. Kehrmann, F. and Saager, A., *Ber. Deut. Chem. Ges.* **35**, 341 (1902).
4. Stránský, Z., Kotouček, M., Stužka, V., and Krbečková, A., *Chem. Ber.* **101**, 201 (1968).
5. Fischer, O. and Hepp, E., *Ber. Deut. Chem. Ges.* **36**, 1807 (1903).
6. Thorpe, J. F., *J. Chem. Soc.* **91**, 324 (1907).
7. Pike, J. A. and Goode, G. G., *Anal. Chim. Acta* **39**, 1 (1967).
8. Middlebrook, R. D., *Proceedings of the IRE*, pp. 1502—1509 (1957).
9. Arthur, P. and Donahue, J. F., *Anal. Chem.* **24**, 1612 (1952).

10. Parsons, J. S. and Seaman, W., *Anal. Chem. 27*, 210 (1955).
11. Dobychin, S. L. and Zozulya, A. P., *Zh. Anal. Khim. 17*, 448 (1962).
12. Číhalík, J., *Potenciometrie.* (Potentiometry.) P. 65. Czechoslovak Academy of Sciences, Prague, 1961.
13. Eckschlager, K., *Chyby chemických rozborů.* (Errors in Chemical Analyses.) P. 98. Státní nakladatelství technické literatury. (State Publishing House of Technical Literature.) Prague, 1971