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APPLICATION OF CERIC PERCHLORATE TO TITRATION OF AMIDES

Ceric perchlorate, introduced to chemical analysis by Smith and Getz [1], is increasingly applied to the titration of both inorganic and organic compounds [2-7]. Its high oxidizing potential (1.7 V) and the high stability of seric perchlorate solution [1] have made it possible to develop methods of titrating amides.

However, the methods employed thus far, i. e. argentometry and alkacymetry [8] make it possible to titrate only some amides, such as e. g. sulfamides, while bromianometry - applied to the titration of acrylic acid amide [9] - does not yield very precise results (margin of error ±2.0%). Gas chromatography, on the other hand, employed in the titration of aliphatic acid amides and acrylic acid amide [10], is of little use in the titration of low-volatility amides, such as e. g. sulfamides.

The cerometric method proposed in the present work makes it possible to determine very small amounts of amides (milligrams) with high precision (margin of error less than 1%).

EXPERIMENTAL

Reagents and solutions

A ~ 0.1 mol./dcm^3 solution of ceric perchlorate in 1.0 mol./ /dm^3 solution of perchloric acid was prepared following the procedure of Smith and Getz [1].

The solution was titrated by the amperometric method using titrated solution of sodium oxalate without e. m. f. applied [2, 3]. The compounds employed were:

Sodium oxalate	p. p. a.	titrated 0.05 mol./dm^3 solution
Perchloric acid	p. p. a.	9.56 mol./dm^3 (Analar)
Acrylic acid amide	p. p. a.	(BDH Chemicals Ltd. Poole)
Malonic acid amide	p. p. a.	(ICN K and Laboratories)
Tartaric acid amide	p. p. a.	(ICN K and Laboratories)
Sulfanil acid amide	p. p. a.	(POCh - Gliwice)

The above amides were twice crystallized and their melting points were determined; they were 356.5-357 K for acrylic acid amide, 442-443 for malonic acid amide, 459-460 for tartaric acid amide, and 437-438 for sulfanil acid amide.

Standard 0.01 mol./dcm^3 solutions of these amides were made using water distilled twice under laboratory conditions.

Titration

0.8-3.0 milimole of ceric perchlorate and an appropriate amount of perchloric acid was poured into 100 ml flasks which were supplied with polished stoppers. The flasks were heated in a UTU thermostate up to a predetermined temperature and a required amount of water solution of the given amide was added from a burette. After the passage of an appropriate amount of time (determined experimentally), the excess of ceric perchlorate was determined by the amperometric method [2, 3].

The measuring apparatus consisted of an indicator electrode (0.1 cm^2 platinum microelectrode), reference electrode (saturated calomel electrode), electrolytic key filled with saturated solution of sodium nitride, galvanometer sensitive to 2.10^{-8} with a measuring range of 1.5×10^{-6} A (RFT) and a shunt (decade 10 kΩ). The end-point of titration was established graphically from the intersection by two straight lines in the coordinate system $I = f(V)$, where V is the volume of the added sodium oxalate.

RESULTS AND CONCLUSIONS

The end products of oxidation with ceric perchlorate of acrylic acid amide, malonic acid amide, and tartaric acid amide were formic acid, carbon dioxide, and ammonium perchlorate, while oxidation of sulfanil acid amide additionally yielded sulfuric acid. The presence of formic acid was established in the following way: a sample of the postreaction mixture was neutralized with excess potassium hydroxide, the precipitate of cerium (III) and cerium (IV) hydroxides and of potassium perchlorate were filteved, and UV spectra were made on a Spekord UV-VIS spectrometer. The absorbability maximum on the spectrum obtained coincided with the maximum on the spectrum of water solution of potassium formate ($\lambda = 210$ nm).

The presence of ammonium and sulfate ions in the post-reaction mixture was confirmed by appropriate qualitative tests. Carbon dioxide given off in the process was identified in a reaction with barit water.

It was also found that oxidation of acrylic acid amide involves an 8-electron transformation, oxidation of malonic and tartaric acid amides involves a 6-electron transformation, and oxidation of sulfanil acid amide involves a 24-electron transformation.

Thus, oxidation of the amides under study with ceric perchlorate can be represented as:

$$CH_2 = CH - CO - NH_2 + 8\ Ce^{4+} + 5\ H_2O \longrightarrow$$
$$8Ce^{3+} + CO_2 + 2\ HCOOH + NH_4^+ + 7\ H^+$$

$$H_2N - OC - CH_2 - CO - NH_2 + 6\ Ce^{4+} + 4\ H_2O \longrightarrow$$
$$6\ Ce^{3+} + 2\ CO_2 + HCOOH + 2\ NH_4^+ + 4\ H^+$$

$$H_2N - OC - C(OH)H - C(OH)H - CO - NH_2 + 6\ Ce^{4+} + 4\ H_2O \longrightarrow$$
$$6\ Ce^{3+} + 2\ CO_2 + HCOOH + 2\ NH_4^+ + 4\ H^+$$

$$H_2N - C_6H_4 - SO_2 - NH_2 + 24\ Ce^{4+} + 14\ H_2O \longrightarrow$$
$$24\ Ce^{3+} + 4\ CO_2 + 2\ HCOOH + 2\ NH_4^+ + SO_4^{2-} + 24\ H^+$$

The conditions under which the titrations were made are summarized in tab. 1.

Table 1

Conditions under which titrations were made

Amide	Oxidizer reducer ratio (molal)	Concentration of $HClO_4$ (in mixture A)	Reaction temperature	Reaction time (hrs)
Acrylic acid amide	20 : 1	5 mol./dcm^3	333 K	0.5
Malonic acid amide	15 : 1	2 mol./dcm^3	298 K	0.5
Tartaric acid amide	15 : 1	2 mol./dcm^3	298 K	0.5
Sulfanil acid amide	40 : 1	3 mol./dcm^3	343 K	2

Five titrations were made for each amide; the results and statistical analyses are collected in tab. 2.

Table 2

Statistical analyses of the results of determination of the mentioned amides by help of cerium (IV) perchlorate

Amide	Sample for anolyze [mg]	Obtained results [mg]	Mean average value	Mean percent error	s [mg]	$\pm t_{0,95} \cdot \bar{s}$ [mg]	s_r [%]
1	2	3	4	5	6	7	8
Acrylic acid amide	3.265	3.248-3.260	3.256	-0.28	0.005	±0.006	0.15
	4.480	4.440-4.465	4.454	-0.58	0.011	±0.014	0.25
	8.885	8.797-8.880	8.830	-0.62	0.032	±0.040	0.36
Malonic acid amide	4.254	4.229-4.389	4.270	+0.37	0.027	±0.033	0.63
	8.508	8.483-8.553	8.525	+0.20	0.47	±0.058	0.55
	17.02	16.94 -17.01	17.01	-0.06	0.080	±0.099	0.47

Table 2 (condt.)

1	2	3	4	5	6	7	8
Tartaric acid amide	6.165	6.142-6.208	6.173	+0.13	0.033	±0.041	0.53
	12.33	12.18-12.33	12.23	-0.81	0.059	±0.073	0.48
	16.03	15.83-16.08	15.95	-0.50	0.089	±0.110	0.56
Sulfanil acid amide	1.794	1.774-1.796	1.790	-0.22	0.010	±0.012	0.56
	3.588	3.552-3.566	3.550	-1.06	0.011	±0.014	0.31
	5.382	5.306-5.376	5.336	-0.85	0.025	±0.031	0.47

The results obtained indicate that the method permits precise titration to be made. Furthermore, the method is simple and no sophisticated apparatus is required.

Summary

A cerometric method for titrating the amides of acrylic, malonic, tartaric, and sulfanil acids is proposed. Also described is a way of identifying formic acid in water solution with perchloric acid, cerium (III) perchlorate and cerium (IV) perchlorate. The method permits relatively precise determinations, is quite simple to employ, and does not require any sophisticated apparatus.

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ZASTOSOWANIE NADCHLORANU CEROWEGO DO ILOŚCIOWEGO OZNACZANIA AMIDÓW

W niniejszej pracy przedstawiono metodę cerometrycznego oznaczania amidów kwasów: akrylowego, malonowego, winowego i sulfanilowego. Opracowano również sposób zidentyfikowania kwasu mrówkowego w wodnej mieszaninie z kwasem nadchlorowym, nadchloranem cerowym i cerawym.

Zaproponowana metoda jest stosunkowo dokładna, a jednocześnie prosta w stosowaniu i nie wymaga skomplikowanej aparatury.

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ИСПОЛЬЗОВАНИЕ ПЕРХЛОРАТА ЦЕРИЯ (IV) К КОЛИЧЕСТВЕННОМУ ОПРЕДЕЛЕНИЮ АМИДОВ

В данной работе представленый метод церометрического определения амидов кислом: акриловой, малоновой, винной и сульфаниловой. Обработаный также метод определения муравийной кислоты в водной смеси с перхлоровой кислотой и перхлоратами церия (IV) и церия (III).

Предложенный метод является тогным и простом в употреблении. Не нужна тоже сложная аппаратура.