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CEROMETRIC DETERMINATION OF ALLYL ALCOHOL
AND ITS DERIVATIVES

A method has been developed of determining allyl alcohol and its derivatives using cerium perchlorate in aqueous solutions of perchloric acid. This method relies upon results arising from the kinetic investigations concerning the reduction of cerium (IV) by the compounds upon present consideration. An excess of oxidizer was determined by the amperometric method without the external potential.

There is no record in chemical literature concerning the method of quantitative determination of allyl alcohol derivatives by means of its oxidation with the use of cerium perchlorate. Only in the paper [1] cerium sulphate in the mixture of sulphuric and acetic acids has been used for the determination of acrolein. An excess of oxidizer has been titrated using the solution of Mohr's salt where the ferroine was used as an indicator. Other derivatives have been determined by means of bromo- and iodometric method [2-4], mercurometric method [5] spectrophotometrically [8, 9] or chromatographically [10-13]. The above method usually concern the single compounds, while there is no method allowing the determination of more number of the derivatives. The results of earlier investigations concerning the reactions of allyl alcohol and its derivatives, with cerium perchlorate in solutions of perchloric acid [14, 15] show the possibility of an application of this oxidizer for the quantitative determination of these compounds.

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Experimental

Reagents and Solutions

Solution of cerium perchlorate 0.865 mole/dm^3 in 6 mole/dm^3 perchloric acid was prepared according to the recipe of Smith and Getz [16]. For that purpose 700 g of cerous chloride was dissolved in 600 cm^3 of triply distilled water. Next, the cerous chloride was performed into cerous perchlorate by the step adding of 72% perchloric acid to the solution being kept in a boiling state. The adding of perchloric acid was stopped when the white smokes had appeared over the reaction mixture and the test with silver nitrate had not indicate the presence of chloride ions. The obtained solution was electrolytically oxidized applying the current 2.5-4 A and its voltage 6-8 V. The platinum plate of the surface 40 cm^2 was standing for the anode, while the cathode was in a form of winded platinum wire of the surface 4 cm^2 .

The end of oxidation was determined in the manner of titration the samples of an oxidized solution with the use of sodium oxalate solution as a titrant by means of amperometric method without the external potential [17]. The concentration of perchloric acid in cerium perchlorate was determined alkacimetrically [18].

The cerium salts in not to high acidic solutions ($\text{pH} > 1$) decompose via the hydrolysis yielding the yellow precipitate of cerium hydroxide, while the cerous ones yield the hydroxide precipitate with $\text{pH} = 5$. Maintaining the above facts, the cerium ions have been reduced to cerous by sodium oxalate and next titrated by the sodium hydroxide solution as a titrant up to the appearance of opacity caused by cerous hydroxide.

Sodium oxalate solution - 0.05 mole/dm^3

Perchloric acid solution - 10.8 mole/dm^3

Allyl alcohol, acrylic acid, acrylic aldehyde solutions 0.1 mole/dm^3 .

These compounds were distilled in order to remove the slight additions of stabilizers used against polymerization. The collected fractions had the boiling points and refractive indexes corresponding to literature data.

Crotylic alcohol, crotonic aldehyde, crotonic acid solutions 0.1 mole/dm^3 were prepared from the weighted portions of these com-

pounds being previously purified by distillation (alcohol, aldehyde or crystallisation acid).

Methyl crotonate solution 0.05 mole/dm^3 in a 3 mole/dm^3 perchloric acid solution.

β, β -dimethylacrylic acid was obtained from the mesitylene oxide by means of modified hypobromate method. The solution 0.1 mole/dm^3 .

Procedure

5 mole of cerium perchlorate were introduced into a measuring flask with an appropriate amount of perchloric acid. Water was added to the solution and after the appropriate temperature had been obtained in the thermostat, a specified quantity of reducing agent was added (Table 1). The volume of reaction mixture was 0.1 dm^3 . The time of reaction was determined experimentally.

In 10 min intervals, 10 cm^3 samples of the reaction mixture were taken in which the non-reacted cerium (IV) was titrated using sodium oxalate solution as a titrant.

The equivalent point of titration was determined by the amperometric method without external potential applied. The oxidation process was regarded as completed when the quantity of non reacted oxidizer did not change even the reaction was allowed to continue. Five series of measurements were made for each reductor. The obtained results with its statistical estimation are presented in Table 1.

Discussion

Taking into account the quantities of cerium (IV) used for the obtaining the final products and its amounts [14, 15] it was pointed out that the reaction of the complete oxidation of the compounds upon present consideration can be introduced according to the following equations:

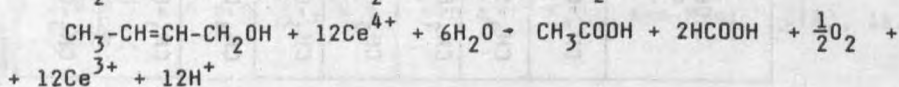
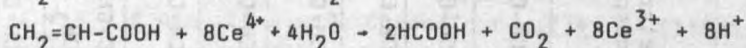
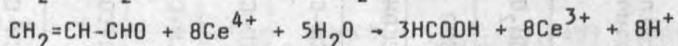
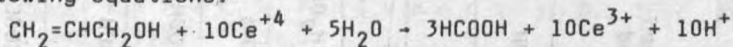
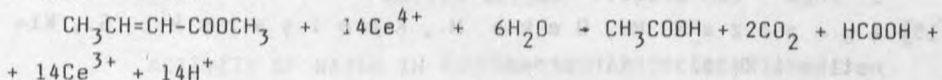
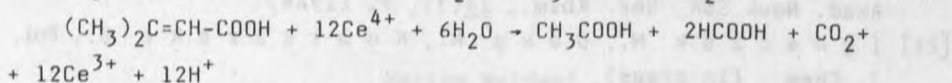
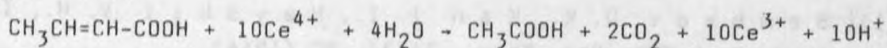
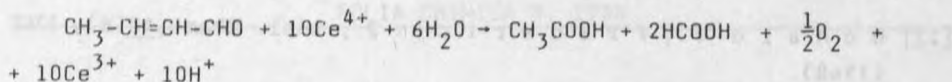


Table 1

Statistical evaluation of the results of determination of allyl alcohol and its derivatives with cerium perchlorate as an oxidizer

Determined compound	Reaction time min	Temperature K	C_{HClO_4} $\text{mol} \cdot \text{dm}^{-3}$	Amount used [mg]	Mean obtained \bar{x} mg	Mean relative error %	Standard deviation $S = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n - 1}}$	Mean standard $\bar{S} = \frac{s}{\sqrt{n}}$	Confidence interval 0.95 $\pm ts$
$\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$	60	298	2.00	5.8 11.6	5.75 11.49	-0.86 -0.95	0.052 0.174	0.023 0.078	0.064 0.217
$\text{CH}_2=\text{CH}-\text{CHO}$	20	298	2.00	5.6 11.2	5.56 11.10	-0.71 -0.89	0.064 0.143	0.029 0.064	0.081 0.178
$\text{CH}_2=\text{CH}-\text{COOH}$	60	333	4.00	7.2 14.4	7.12 14.19	-1.11 -1.46	0.153 0.123	0.068 0.055	0.189 0.153
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$	30	298	2.00	7.2 14.4	7.13 14.24	-0.97 -1.11	0.128 0.179	0.057 0.080	0.158 0.222
$\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$	30	298	2.00	7.0 14.0	6.88 13.89	-1.71 -0.79	0.166 0.171	0.074 0.076	0.205 0.211
$\text{CH}_3-\text{CH}=\text{CH}-\text{COOH}$	30	333	2.00	8.6 17.2	8.49 17.11	-1.28 -0.52	0.109 0.158	0.049 0.071	0.136 0.197
$\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}-\text{COOH}$	40	333	4.00	10.0 20.0	10.07 19.92	0.70 -0.40	0.128 0.128	0.057 0.057	0.158 0.158
$\text{CH}_3-\text{CH}=\text{CH}-\text{COOCH}_3$	40	333	2.00	10.0 20.0	9.88 19.88	-0.20 -0.10	0.114 0.095	0.051 0.042	0.142 0.117



The acids: formic and acetic one do not oxidize in the conditions of the present measurements [19-20].

The obtained results in almost all cases involve small negative relative error. This is probably caused by the partial oxidation of the compound studied by the influence of light. In regard to the amounts of the substances used for determinations the values of mean relative error can be considered as relatively small ones. The small relative standard deviation values confirm the accuracy of the proposed method. One is also in position to mention that our method is rather simple and it does not require the use of any sophisticated apparatus.

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CEROMETRYCZNE OZNACZANIE ALKOHOLU ALLILOWEGO I JEGO POCHODNYCH

Opracowano metodę oznaczania alkoholu allilowego i jego pochodnych przy użyciu nadchloranu cerowego w wodnych roztworach kwasu nadchlorowego. Wykorzystano w tym celu kinetyczną metodę ustalonego czasu reakcji oraz metodę amperometryczną do określania ilości prze-reagowanego ceru (IV).