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CEROMETRIC DETERMINATION OF PHENOL AND SOME OF ITS DERIVATIVES

A method has been developed of determining phenol and its de-
rivatives using cerium perchlorate in aqueous perchloric acid so-
lution. The procedure takes advantage of the kinetic method of
fixed reaction time and of the amperometic method of determining
the amount of reacted cerium (IV).

Oxidation of phenols with various oxidizers has received a
lot of attention. In most cases the process is held to   be non-
stoichiometric. The   end products are mostly ring derivatives of
the compounds studied, usually their mixtures which are difficult
to separate and identify [1-5]. The present study is part   of
a larger investigation devoted to oxidation of phenols with   ce-
rium perchlorate in perchloric acid medium. Cerium   perchlorate
exhibits high oxidizing potential (1.71 V) and its other proper-
ties include high stability of its solutions and the   fact that
perchlorate and cerium ions do not form complexes junction [6].
It has been found that cerium (IV) in $HClO_4$ solution oxidizes
phenol and its derivatives in a destructive way, and   the   re-
sults of stoichiometric measurements show that   it con be used
for quantitative determination of these compounds.

Experimental

Reagents and solutions

Solution of cerium perchlorate 1 mole/dm^3 in 2 mole/dm^3 per-
chloric acid was prepared in accordance with   S m i t h   and
G e t z [7]. Cerium perchlorate concentration was determined by
the amperometric method using titrated sodium oxalate solution [8].
The concentration of perchloric acid in cerium   perchlorate so-

lution was determined alkacimetrically with cerium (IV) having first been reduced to cerium (III);

Sodium oxalate solution - 0.05 mole/dm^3

Perchloric acid solution - 9.5 mole/dm^3

Aqueous solution of phenol, p-cresol, p-nitrophenol, p-hydroxybenzoic acid and picric acid - 10^{-2} mole/dm^3.

2,6-dinitrophenol solution - 6.25 x 10^{-3} mole/dm^3

The phenols used were purified by distillation (phenol and p-cresol), crystalization from water (p-nitrophenol, p-hydroxybenzoic acid), or from dilute acid (2,6-dinitrophenol and picric acid). The water employed had been distilled twice.

Procedure

5 mmole cerium perchlorate were introduced into the measuring flask together with an amount of perchloric acid such that its concentration in the reaction medium was 2 mole/dm^3. Water was added to the solution and, after appropriate temperature had been obtained in the thermostat, a specified quantity of the solution of the reducing agent was added (Tab. 1). The volume of the reaction mixture was 0.1 m^3. The time of the reaction was determined experimentally. Samples of the reaction mixture were taken in which the reaction was stopped by adding 10 ml of 0.05 mole/dm^3 sodium oxalate solution. The excess of unreacted sodium oxalate was titrated back with cerium perchlorate solution; the equivalent point of titration was determined by the amperometric method with no external e.m.f applied [8]. The quantity of cerium (IV) which had reacted with the appropriate reducing agent corresponded in this case to the number of mmoles of cerium perchlorate used for titration of the unreacted sodium oxalate. The oxidation process was regarded as completed when the quantity of unreacted cerium (IV) did not change even though the reaction was allowed to continue. Three series of measurements were made for each phenol studied. The results obtained and the statistics are presented in Tab. 1.

Discussion

The measurements performed show that complete oxidation of phenol and its derivatives with cerium (IV) in perchloric acid
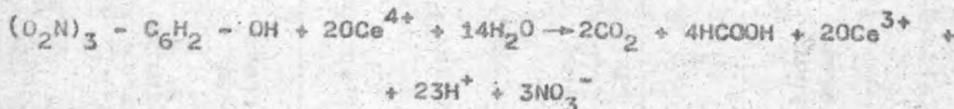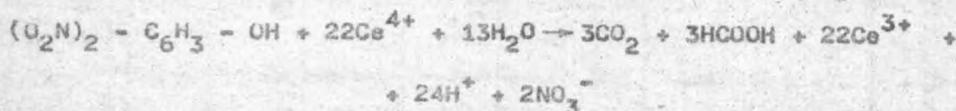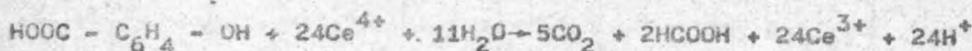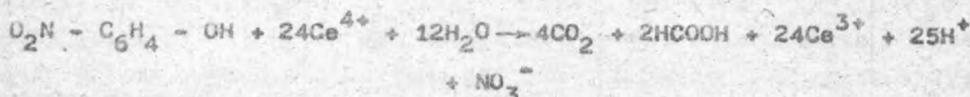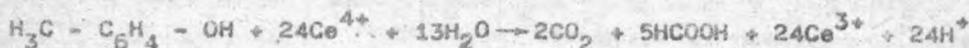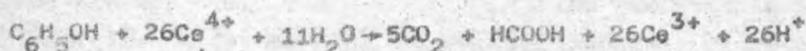
Statistical evaluation of the results of determination of phenol and some its derivatives
with cerium perchlorate as the oxidizer

Determind compound	Reaction time	Tempera- ture K	Amount used mg	Mean obtained $\bar{X}$ mg	Mean relative error	SD for indivi- dual re- sults $\bar{s}$ mg	Signifi- cance interval of the mean $\pm t_{0.95} \cdot s$ mg	$s_r \cdot 100$ %
1	2	3	4	5	6	7	8	9
phenol	60	343	5.00	4.96	-0.80	0.015	0.016	0.12
			8.00	7.97	-0.13	0.077	0.080	0.04
			10.00	9.93	-0.70	0.028	0.029	0.11
p-cresol	120	343	7.24	7.21	-0.41	0.080	0.084	0.44
			12.00	11.95	-0.42	0.030	0.031	0.10
			16.36	16.31	-0.31	0.076	0.080	0.19
p-nitrophenol	120	343	6.00	5.95	-0.83	0.047	0.049	0.32
			9.00	8.89	-0.11	0.0063	0.0067	0.029
			12.00	11.91	-0.75	0.084	0.088	0.29
p-hydroksy- benzoic acid	120	343	2.76	2.77	0.36	0.040	0.042	0.61
			4.14	4.08	-1.45	0.023	0.024	0.23
			8.28	8.14	-1.69	0.089	0.093	0.44
2,6-dinitro- phenol			5.75	5.73	-0.35	0.053	0.056	0.38
			8.63	8.56	-0.81	0.083	0.087	0.40
			11.50	11.42	-0.70	0.11	0.12	0.40
picric acid	10	293	4.58	4.54	-0.87	0.059	0.063	0.52
			6.87	6.82	-0.73	0.022	0.023	0.13
			9.16	9.09	-0.76	0.10	0.11	0.18

solution does not take place with satisfactory rate until the temperature is raised. It was found in earlier research that the rates of these reaction are limited by the oxidation processes involving the intermediate compound [9]. The only exception is picric acid which undergoes oxidation at room temperature, the rate of the process being determined by the transfer of the first electron [10]. The end products of this reaction are carbon dioxide and formic acid detected in the reaction medium by qualitative tests. It is noteworthy that formic acid does not undergo oxidation with cerium (IV) under the conditions and during the time of the present measurements [11-13]. Its presence was confirmed by chromatography; the chromatographs of the ether extracts of the postreaction mixtures corresponded to that of the standard $HCOOH - (C_2H_5)_2O$ sample.

Measurements were also performed of the quantity of carbon dioxide given off in the different oxidation reactions. On the basis of the results obtained the following reaction schemes can be proposed for the oxidation of phenol and its derivatives with cerium (IV) in perchloric acid solution:

$$C_6H_5OH + 26Ce^{4+} + 11H_2O \rightarrow 5CO_2 + HCOOH + 26Ce^{3+} + 26H^+$$

$$H_3C - C_6H_4 - OH + 24Ce^{4+} + 13H_2O \rightarrow 2CO_2 + 5HCOOH + 24Ce^{3+} + 24H^+$$

$$O_2N - C_6H_4 - OH + 24Ce^{4+} + 12H_2O \rightarrow 4CO_2 + 2HCOOH + 24Ce^{3+} + 25H^+ + NO_3^-$$

$$HOOC - C_6H_4 - OH + 24Ce^{4+} + 11H_2O \rightarrow 5CO_2 + 2HCOOH + 24Ce^{3+} + 24H^+$$

$$(O_2N)_2 - C_6H_3 - OH + 22Ce^{4+} + 13H_2O \rightarrow 3CO_2 + 3HCOOH + 22Ce^{3+} + 24H^+ + 2NO_3^-$$

$$(O_2N)_3 - C_6H_2 - OH + 20Ce^{4+} + 14H_2O \rightarrow 2CO_2 + 4HCOOH + 20Ce^{3+} + 23H^+ + 3NO_3^-$$

In most cases the results of the determinations collected in Tab. 1 involve small negative relative error. This is probably due to partial oxidation of the compounds studied under the in-

fluence of light and atmospheric oxygen. Considering the amounts
of the substances used for determinations, the magnitudes of mean
relative error may be regarded as virtually negligible. The small
relative standard deviation values testify to the accuracy of the
method proposed. It is simple, does not require the use of any
sophisticated apparatus, and permits comparatively accurate de-
terminations of the compounds involved.

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CEROMETRYCZNE OZNACZENIE FENOLU I NIEKTÓRYCH JEGO POCHODNYCH

Opracowano metodę oznaczania fenolu i jego pochodnych przy użyciu nadchloranu cerowego w wodnym roztworze kwasu nadchlorowego. Wykorzystano w tym celu kinetyczną metodę ustalonego czasu reakcji oraz metodę amperometryczną do określenia ilości przereagowanego ceru (IV).

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ЦЕРОМЕТРИЧЕСКИЕ ОПРЕДЕЛЕНИЕ ФЕНОЛА И ЕГО НЕКОТОРЫХ ПРОИЗВОДНЫХ

Разработан метод определения фенола и его производных перхлоратом церия в водном растворе хлорной кислоты. Применено для этой цехи кинетический метод установившего время реакции а также амперометрический способ для определения количества реагирующего церия (IV).