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CEROMETRIC DETERMINATION OF PHENOL AND SOME OF ITS DERIVATIVES

A method has been developed of determining phenol and its derivatives using cerium perchlorate in aqueous perchloric acid solution. The procedure takes advantage of the kinetic method of fixed reaction time and of the amperometric 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 cerium perchlorate in perchloric acid medium. Cerium perchlorate exhibits high oxidizing potential (1.71 V) and its other properties 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 HClO₄ solution oxidizes phenol and its derivatives in a destructive way, and the results of stoichiometric measurements show that it can be used for quantitative determination of these compounds.

Experimental

Reagents and solutions

Solution of cerium perchlorate 1 mole/dm³ in 2 mole/dm³ perchloric acid was prepared in accordance with Smith and Getz [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-
olution was determined alkacimetrically with cerium (IV) hav­
ing first been reduced to cerium (III);
Sodium oxalate solution - 0.05 mole/dm³
Perchloric acid solution - 9.5 mole/dm³
Aqueous solution of phenol, p- cresol, p-nitrophenol, p-hydro­
xybenzoic acid and picric acid - 10⁻² mole/dm³.
2,6-dinitrophenol solution - 6.25 x 10⁻³ mole/dm³
The phenols used were purified by distillation (phenol and
p-cresol), crystallization from water (p-nitrophenol, p-hydroxy­
benzoic 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/dm³. 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 m³. The time of the reaction was deter­
mined experimentally. Samples of the reaction mixture were taken
in which the reaction was stopped by adding 10 ml of 0.05 mole/dm³
sodium oxalate solution. The excess of unreacted sodium oxalate
was titrated back with cerium perchlorate solution; the equiva­
 lent 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 phae­
nol studied. The results obtained and the statistics are pre­
sented in Tab. 1.

Discussion

The measurements performed show that complete oxidation of
phenol and its derivatives with cerium (IV) in perchloric acid
### Table 1

Statistical evaluation of the results of determination of phenol and some of its derivatives with cerium perchlorate as the oxidizer.

<table>
<thead>
<tr>
<th>Determined compound</th>
<th>Reaction time</th>
<th>Temperature K</th>
<th>Amount used mg</th>
<th>Mean obtained X mg</th>
<th>Mean relative error</th>
<th>SD for individual results σ mg</th>
<th>Significance interval of the mean $t_{0.95} \cdot \sigma mg</th>
<th>95%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>phenol</strong></td>
<td>60</td>
<td>343</td>
<td>5.00</td>
<td>4.96</td>
<td>-0.80</td>
<td>0.015</td>
<td>0.016</td>
<td>0.12</td>
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<td></td>
<td>6.00</td>
<td></td>
<td>8.00</td>
<td>7.97</td>
<td>-1.33</td>
<td>0.077</td>
<td>0.080</td>
<td>0.11</td>
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<td></td>
<td>10.00</td>
<td></td>
<td>10.00</td>
<td>9.93</td>
<td>-0.70</td>
<td>0.028</td>
<td>0.029</td>
<td>0.04</td>
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<td><strong>p-cresol</strong></td>
<td>120</td>
<td>343</td>
<td>7.24</td>
<td>7.21</td>
<td>-0.41</td>
<td>0.080</td>
<td>0.084</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>12.00</td>
<td></td>
<td>12.00</td>
<td>11.95</td>
<td>-0.42</td>
<td>0.030</td>
<td>0.031</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>16.36</td>
<td></td>
<td>16.30</td>
<td>16.31</td>
<td>-0.31</td>
<td>0.076</td>
<td>0.080</td>
<td>0.19</td>
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<tr>
<td><strong>p-nitrophenol</strong></td>
<td>120</td>
<td>343</td>
<td>6.00</td>
<td>5.95</td>
<td>-0.83</td>
<td>0.047</td>
<td>0.049</td>
<td>0.32</td>
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<tr>
<td></td>
<td>9.00</td>
<td></td>
<td>9.00</td>
<td>8.89</td>
<td>-1.11</td>
<td>0.0063</td>
<td>0.0067</td>
<td>0.029</td>
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<tr>
<td></td>
<td>12.00</td>
<td></td>
<td>12.00</td>
<td>11.91</td>
<td>-0.75</td>
<td>0.076</td>
<td>0.084</td>
<td>0.29</td>
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<tr>
<td><strong>p-hydroxybenzoic acid</strong></td>
<td>120</td>
<td>343</td>
<td>2.76</td>
<td>2.77</td>
<td>0.36</td>
<td>0.040</td>
<td>0.042</td>
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<td>4.14</td>
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<td>4.08</td>
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<td>0.024</td>
<td>0.23</td>
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<tr>
<td></td>
<td>8.28</td>
<td></td>
<td>8.28</td>
<td>8.14</td>
<td>-1.69</td>
<td>0.089</td>
<td>0.093</td>
<td>0.44</td>
</tr>
<tr>
<td><strong>2,6-dinitrophenol</strong></td>
<td>10</td>
<td>293</td>
<td>5.75</td>
<td>5.73</td>
<td>-0.35</td>
<td>0.053</td>
<td>0.056</td>
<td>0.38</td>
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<tr>
<td></td>
<td>5.75</td>
<td></td>
<td>5.75</td>
<td>5.73</td>
<td>-0.35</td>
<td>0.053</td>
<td>0.056</td>
<td>0.38</td>
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<td></td>
<td>9.63</td>
<td></td>
<td>9.63</td>
<td>8.56</td>
<td>-0.81</td>
<td>0.083</td>
<td>0.087</td>
<td>0.40</td>
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<td></td>
<td>11.50</td>
<td></td>
<td>11.50</td>
<td>11.42</td>
<td>-0.70</td>
<td>0.11</td>
<td>0.12</td>
<td>0.40</td>
</tr>
<tr>
<td><strong>picric acid</strong></td>
<td>10</td>
<td>293</td>
<td>4.58</td>
<td>4.54</td>
<td>-0.67</td>
<td>0.059</td>
<td>0.063</td>
<td>0.52</td>
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<td></td>
<td>6.87</td>
<td></td>
<td>6.87</td>
<td>6.82</td>
<td>-0.73</td>
<td>0.022</td>
<td>0.023</td>
<td>0.13</td>
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<td></td>
<td>9.16</td>
<td></td>
<td>9.16</td>
<td>9.09</td>
<td>-0.76</td>
<td>0.10</td>
<td>0.11</td>
<td>0.18</td>
</tr>
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</table>
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\(_2\)H\(_3\))\(_2\)O 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:

\[
\begin{align*}
C_6H_5OH & \rightarrow 26Ce^{4+} + 11H_2O \rightarrow 5CO_2 + HCOOH + 26Ce^{3+} + 26H^+ \\
H_3C - C_6H_4 - OH & \rightarrow 24Ce^{4+} + 13H_2O \rightarrow 2CO_2 + 5HCOOH + 24Ce^{3+} + 24H^+ \\
O_2N - C_6H_4 - OH & \rightarrow 24Ce^{4+} + 12H_2O \rightarrow 4CO_2 + 2HCOOH + 24Ce^{3+} + 25H^+ \\
HCOOH & \rightarrow 24Ce^{4+} + 11H_2O \rightarrow 5CO_2 + 2HCOOH + 24Ce^{3+} + 24H^+ \\
(O_2N)_2 & \rightarrow C_6H_3 - OH + 22Ce^{4+} + 13H_2O \rightarrow 3CO_2 + 3HCOOH + 22Ce^{3+} + 24H^+ + 2NO_3^- \\
(O_2N)_3 & \rightarrow C_6H_2 - OH + 20Ce^{4+} + 14H_2O \rightarrow 2CO_2 + 4HCOOH + 20Ce^{3+} + 23H^+ + 3NO_3^- \\
\end{align*}
\]

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 determinations of the compounds involved.

References


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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).

ЦЕРОМЕТРИЧЕСКИЕ ОПРЕДЕЛЕНИЕ ФЕНОЛА И ЕГО НЕКОТОРЫХ ПРОИЗВОДНЫХ

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