Redox Potential Values of Br⁺/Br⁻ System with Regard to the Use of N-Bromosuccinimide as Titrant

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Redox potential of Br⁺Br⁻ system when N-bromosuccinimide is used as a titrant is described in water and aqueous solution containing acids and base.

1 Introduction

The oxidizing property of N-bromosuccinimide has been used for the determination of various substances(11-13). These oxidations were selective as well as general. Until now the selection of conditions was made just by hit and trial. It was not known what would be the oxidizing potential of N-bromosuccinide in the given conditions. There was not any systematic study available on the redox potential of Br⁺Br⁻ system with regard to the use of N-bromosuccinimide in various conditions.

In this paper it was decided to study the redox potential of the Br⁺/Br⁻ system in aqueous medium, acetic acid, HCl, H₂SO₄, and Na₂CO₃ of various molarities. These results of redox potentials of Br⁺/Br⁻ system when N-bromosuccinimide is used as a titrant, will help the analytical chemist to judge before hand which substances possibly can be oxidized in the given system.

2 Experimental

2.1 Apparatus

All potential measurements were made with Radelkis Universal pH meter, type: OP 204/1. Platinum strip indicating electrode was used against saturated calomel reference electrode.

2.2 Reagents

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N-bromosuccinimide −0.01 M solution of recrystallized N-bromosuccinimide was prepared in distilled and deionized water.

Potassium bromide −0.01 M solution of recrystallized potassium bromide was made in distilled and deionized water. Similarly the CH₃COOH, Na₂CO₃, HCl, and H₂SO₄ were also of analytical grade and the dilutions to required molarities were made in distilled and deionized water.

3 Procedure

The potentiometer was standardized as given in the manual and then checked with the known system of [Fe(CN)₆]₃⁻/[Fe(CN)₆]₄⁻. To a 100 ml beaker a 20 ml solution of 0.01 M N-bromosuccinimide was added and then the electrodes were dipped into it and 20 ml of 0.01 M KBr were added. After magnetic stirring the potential was measured. These values were then changed to standard potentials with respect to standard hydrogen electrode. When the potential in acidic or alkali medium was measured the molarities of acids or bases were calculated from the total volume in the beaker.

4 Results and Discussion

The redox potential of Br⁺/Br⁻ system was first measured in aqueous medium because water is almost a universal solvent and most of the determinations are done in it. The potential was measured from a total volume of 40 ml in which 20 ml of 0.01 M N-bromosuccinimide and 20 ml of 0.01 M KBr were mixed. The redox
The Table 1 The values of redox potential of the Br⁺/Br⁻ system in different aqueous media at 25°C

<table>
<thead>
<tr>
<th>Aqueous medium</th>
<th>Molarity</th>
<th>Redox potential (V)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>-</td>
<td>+1.103</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.1</td>
<td>+1.142</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>+1.146</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>+1.148</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>0.1</td>
<td>+1.170</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>+1.168</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>+1.136</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>0.1</td>
<td>+1.156</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>+1.144</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>+1.139</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>0.1</td>
<td>+0.828</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>+0.804</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>+0.796</td>
</tr>
</tbody>
</table>

* The reliability of results is ± 20 mV.

The redox potentials in aqueous medium with several concentrations of acetic acid were measured and molarity of CH₃COOH was calculated from the total volume in the potential measuring beaker. As the molarity of the acid increases the redox potential of Br⁺/Br⁻ system shows little increase. We have not gone beyond the molarities shown in Table 1 because in general practice these are the workable concentrations.

But the redox potential in aqueous hydrochloric acid medium is certainly greater than that of CH₃COOH. As is clear from Table 1, with increasing concentration of HCl there is decrease in redox potential. This may be due to the increase of hydrogen ion concentration thus decreasing the diffusion of Br⁺ from N-bromosuccinimide.

Similar is the case when the potential was measured in aqueous sulphuric acid.

The redox potential of the system Br⁺/Br⁻ was also measured in alkaline medium and for this, sodium carbonate was selected. As can be seen from the Table 1 that the redox potential is much less in alkaline medium than in acid medium.

The results of all the measurements are summarized in Table 1.

The results in Table 1 show that the redox potential of N-bromosuccinimide in dilute mineral acids is 1.16-1.17 volts and in alkaline medium it is 0.82 volts. This potential is quite high for many determinations. The compounds which have been determined with N-bromosuccinimide are ascorbic acid¹,² thiocyanate³, cysteine⁴, arsenite⁵, stanous⁶, thiosulphate⁷, sulfide⁸, and nitrite⁹. The oxidation potential of ascorbic acid in acidic medium is 0.32 V¹⁰ while the oxidation potential of thiocyanate in acidic medium is 0.77 V¹¹. At pH of 7.0 cysteine has oxidation potential of 0.33 V¹² and arsenite at the same pH has oxidation potential of 0.31 V¹³. Stanous has oxidation potential of 0.15 in acidic medium¹⁴. The oxidation potential of thiosulphate in aqueous medium is 0.4 V¹⁵. Sulfide at pH 6 can be oxidized at 0.14 V¹⁶. The oxidation potential of nitrite in alkaline medium is 0.01 V¹⁷. These potentials are well below the redox potential of N-bromosuccinimide in order to oxidize these compounds.

It shall be remembered that the potentials are represented by the following Nernst equation:

\[ E = E_0 + \frac{RT}{nF} \ln \frac{a_{OX}}{a_{Red}} \]

As the concentrations of reacting species are quite low, in the vicinity of 0.01 M, the activity coefficients of oxidized and reduced forms are taken as unity, therefore, these will be replaced by concentrations. Keeping all these redox potential values in mind N-bromosuccinimide can be used quite carefully and usefully.

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