Determination of 4-Hydroxybiphenyl with N-bromosuccinimide

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Summary: A potentiometric titration method has been used for the determination of 4-hydroxybiphenyl with N-bromosuccinimide (NBS). The organic compound like 4-hydroxybiphenyl is less soluble in aqueous media, while platinum indicator electrode requires aqueous medium for potential measurements. Therefore, a mixed organic-aqueous medium has been used to dissolve 4-hydroxybiphenyl for its determination with N-bromosuccinimide. A linear curve is obtained by plotting peak height (cm) vs. concentration (mg) of 4-hydroxybiphenyl determined. The method is simple, as it requires only readily available laboratory equipment. At moderate concentrations of the analyte, the error is within the range +0.1 to -0.4. However, at lower concentrations, typically a few mg of the analyte, the error range is -3.3 to - 3.6.

Introduction

A number of physical [1], biological [2], chemical methods including various visual titration [3], photoelectric [4], coulometric [5] and potentiometric [6] methods have been developed for analysis of 4-hydroxybiphenyl. But all these require expensive instruments or tedious and time consuming experimentation. Therefore, a simple method is developed for the determination of 4-hydroxybiphenyl with N-bromosuccinimide. The end point is determined potentiometrically employing a calomel reference electrode and a platinum indicator electrode [7]. N-bromosuccinimide is listed as a derivative of 2,5-pyrrolidinedione i.e., 1-bromo-2,5-pyrrolidinedione. N-bromosuccinimide is used as reagent for oxidation of organic compounds. N-bromosuccinimide serves as a source of bromonium ion, (Br^+) or hypobromite of low concentration, and the reaction is free from the side reactions generally associated with the use of hypobromite solutions. N-bromosuccinimide and many other "positive" halogen compounds are available in a high state of purity; they can, therefore, be used as primary standards and the solid reagents are fairly stable [8].

A direct titrimetric method for the determination of phenol in methanol solution by means of 0.1 N N-bromosuccinimide in glacial acetic acid as titrant, applying mercuric chloride catalyst in the presence of sodium acetate and potassium bromide. As soon as the N-bromosuccinimide is in excess, bromine is liberated, and the end point is detected on basis of its depolarizing action on the polarized pair of platinum electrodes [9]. An efficient and mild method for the halogenation of aromatic compounds using N-chloro-, N-bromo-, and N-iodosuccinimide in the presence of ammonium nitrate in acetonitrile was developed [10]. A convenient and efficient procedure for electrophilic aromatic bromination has been developed by mixing of N-bromosuccinimide and an aromatic compound at room temperature on the surface of silica gel mixed with solid anhydrous lithium perchlorate [11].

The kinetics of oxidation of aminoalcohols viz ethanolamine, diethanolamine and triethanolamine by N-bromosuccinimide in alkaline medium have been investigated [12]. N-bromo-succinimide and iodine solution have been used separately for oxidation of vitamin C in orange juice and pharmaceutical preparations. The statistical evaluation has shown that titration with dilute solution ($2.2x10^{-3}$ M) of NBS has produced better results as compared to iodine method [13].

A titrimetric procedure, with a potentiometric control of the end point, is described for the determination of mercaptans with N-bromosuccinimide in a mixed solvent of acetonitrile-methanol [14]. Two methods are described for the determination of tenoxicam and piroxicam. The potentiometric method involves the direct titration of both drugs with N-bromosuccinimide in acid medium and the end point is determined potentiometrically using platinum indicator electrode [15].

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Table-1: Potentiometric determination of 9-20 mg of 0.008 N 4-hydroxybiphenyl solutions with 0.02 NBS (4-Hydroxybiphenyl and 0.02 N NBS were prepared in 16.6 % methyl alcohol in 0.05 N acetic acid).

No	4-Hydroxybiphenyl taken		Equivalents of NBS used		4-Hydroxybiphenyl determined	Peak height	% Error
of obs.	(mg)	(mL)	(mg)	(mL)	(mg)	(cm)	
1	9	18.3	9.43	5.30	9.01	3.3	+0.1
2	14	28.5	14.66	8.20	13.93	5.3	-0.4
3	16	32.5	16.76	9.40	15.96	6.1	-0.2
4	20	40.7	20.95	11.8	20.02	7.4	-0.1

Results and Discussion

The present procedure affords a simple, general method for the determination of 4-hydroxybiphenyl with N-bromosuccinimide, electrometrically and it avoids the complexity of solvent systems often used in such reactions. The potentiometric titrations were performed in acidic, neutral and alkaline medium, using an appropriately constituted cell. Quantitative measurements of 4-hydroxybiphenyl were obtained from first derivative of the sigmoid-shaped curves of 4-hydroxybiphenyl, titrated potentiometrically against a standard solution of N-bromosuccinimide containing 0.178 g/100 mL (1 mM). The sudden change in mV values shows the equivalence point between the two solutions, determined potentiometrically. The results of titration are given in table 1. The sigmoid shape of E vs. V graph gave a peak-shaped ΔE/ΔV vs. V, shown in figure 1.

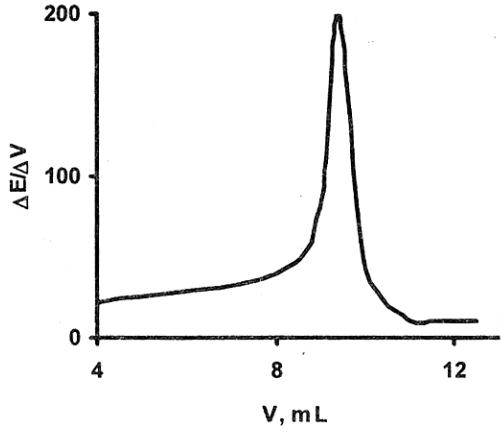

Fig. 1: ΔE/ΔV vs. V, mL curve. 14 mg 4-hydroxybiphenyl with 0.02 N N-bromo-succinimide (both 4-hydroxybiphenyl and NBS are prepared in 16.6% methyl alcohol in 0.05 N acetic acid).

A linear curve obtained by plotting height (cm) vs. concentrations (mg) of 4-hydroxybiphenyl determined is also shown in figure 2.

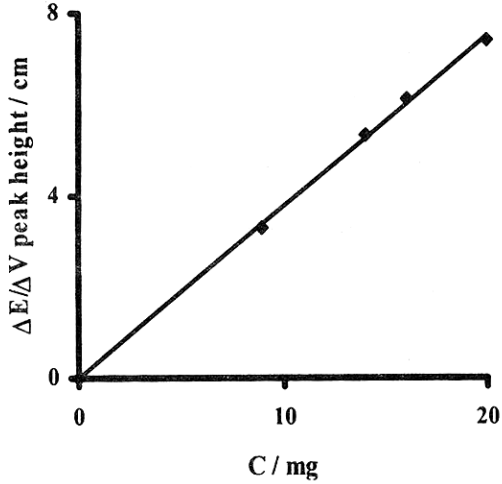

Fig. 2: ΔE/ΔV peak height / cm vs. C / mg. Linear curve of 4-hydroxybiphenyl (mg) determined, against peak height (cm).

The linear regression coefficient of correlation is one and the intercept is –0.001. The results showed that the reaction is quantitative with an error of ± 0.4 to ± 0.5%. The results of equivalents of NBS used (mL) obtained by this potentiometric determination of 4-hydroxybiphenyl solutions, calculated from sigmoid shape graph and inflection point graph are also shown in table 2.

The results of potentiometric determination of 3, 30, 300 mg of 4-hydroxybiphenyl with 0.02N N-bromosuccinimide (both 4-hydroxybiphenyl and 0.02 N NBS are prepared in 10 % and 50 % acetonitrile containing 0.1 M sodium perchlorate) are shown in table 3 and table 4. And the results of titrations in pH 9 solutions are given in table 5.

Labeling experiments have demonstrated that the bromine from the N-bromosuccinimide appeared for the electrophilic aromatic substitution in the 4-hydroxybiphenyl ring. NBS undergoes a two-electron reduction and stoichiometry of the reaction was 1:1 [16].

Table-2: Potentiometric determination of 9-20 mg of 0.008 N 4-hydroxybiphenyl solutions with 0.02 NBS (4-Hydroxybiphenyl and 0.02 N NBS were prepared in 16.6 % methyl alcohol in 0.05 N acetic acid).

No. of obs.	4-Hydroxybiphenyl taken		Equivalents of NBS used (mL) obtained by making		4-Hydroxybiphenyl determined	Peak height (cm)	% Error
	(mg)	(mL)	Sigmoid shape graph	Inflection point graph	(mg)		
1	9	18.3	5.30	5.30	9.01	3.3	+0.1
2	14	28.5	8.20	8.20	13.93	5.3	-0.4
3	16	32.5	9.40	9.40	15.96	6.1	-0.2
4	20	40.7	11.8	11.8	20.02	7.4	-0.1

Table-3: Potentiometric determination of 3, 30, 300 mg of 4-hydroxybiphenyl with 0.02 N N-bromosuccinimide (4-hydroxybiphenyl and 0.02 N NBS were prepared in 10 % acetonitrile).

No of obs.	4-Hydroxybiphenyl taken (mg)	(mL)	Equivalents of NBS used (mg)	(mL)	4-Hydroxybiphenyl determined (mg)	Peak height (cm)	% Error
1	3	taken in 50 mL 10% acetonitrile	3.04	1.7	2.9	12	-3.3
2	30	taken in 50 mL 10% acetonitrile	31.43	17.6	29.92	13.8	-0.2
3	300	taken in 50 mL 10% acetonitrile	315.2	176.5	300.00	13.8	0.0

Table-4: Potentiometric determination of 3, 30, 300 mg of 4-hydroxybiphenyl with 0.02N N-bromosuccinimide (4-hydroxybiphenyl and 0.02 N NBS were prepared in 50 % acetonitrile).

No of obs.	4-Hydroxybiphenyl taken		Equivalents of NBS used		4-Hydroxybiphenyl determined	Peak height	% Error
	(mg)	(mL)	(mg)	(mL)	(mg)	(cm)	
1	3	taken in 50 mL 50% acetonitrile	3.04	1.7	2.89	12.0	-3.6
2	30	taken in 50 mL 50% acetonitrile	31.43	17.6	29.92	13.2	-0.2
3	300	taken in 50 mL 50% acetonitrile	315.2	176.5	300.02	13.8	+0.01

Table 5: Potentiometric determination of 3, 30, 300 mg of 4-hydroxybiphenyl with 0.02N N-bromosuccinimide (4-hydroxybiphenyl and 0.02 N NBS were dissolved in 16.6 % methyl alcohol, pH 9 solution).

No of obs.	4-Hydroxybiphenyl taken (mg)	(mL)	Equivalents of NBS used (mg)	(mL)	4-Hydroxybiphenyl determined (mg)	Peak height (cm)	% Error
1	3	taken in 50 mL pH 9, 16.6% MeOH	3.04	1.7	2.89	12.1	-3.6
2	30	taken in 50 mL pH 9, 16.6% MeOH	31.43	17.6	29.92	12.5	-0.2
3	300	taken in 50 mL pH 9, 16.6% MeOH	315.2	176.5	300.02	12.8	+0.01

A number of other methods, available in the literature, either involve expensive instruments or tedious and time-consuming experimentation. The results obtained by this potentiometric determination of 4-hydroxybiphenyl are also confirmed by other well-known methods [17-19].

Experimental

N-bromosuccinimide, Fluka; 4-hydroxy-biphenyl, Fluka; sodium perchlorate, E-Merck; Acetonitrile, Lederle; silver nitrate, E-Merck; nitric acid, E-Merck; hydrochloric acid, BDH, England. Potassium chloride, acetic acid, and methyl alcohol were of Aldrich and used as received.

Potentiometric titrations were carried out to measure oxidation potential of 4-hydroxybiphenyl in mV for its determination, at platinum electrode. The technique is simple, as it requires only readily available laboratory equipment.

Reference electrode

Silver/silver chloride electrode was used as reference electrode. The silver wire coated with silver chloride and immersed in the potassium chloride solution saturated with silver chloride.

For acetonitrile, silver wire was immersed in 0.1 M sodium perchlorate in acetonitrile.

Indicator electrode

The platinum wire electrode was used as the indicator electrode to measure the redox potential in mV.

PTI-15 digital pH meter was used as potentiometer to measure the potential between the two electrodes.

Reagents

Acetic acid 0.05 N: Glacial acetic acid, 0.3 mL was diluted with distilled water and volume was made up to 100 mL.

Methyl alcohol (16.6%)

Methyl alcohol was prepared by diluting the 20 mL of methyl alcohol up to 120 mL of 0.05 N acetic acid solution.

4-Hydroxybiphenyl solution, 0.008N:

4-Hydroxybiphenyl, 59 mg was dissolved in 120 mL of 16.6% methyl alcohol.

N-bromosuccinimide solution 1 mM (freshly prepared)

N-bromosuccinimide, 0.178 g was dissolved in 100 mL of 16.6% methyl alcohol.

Sodium perchlorate 0.1 M

Sodium perchlorate was dried at 80 °C for 24 hours, and 1.23 g was dissolved in acetonitrile and volume was made up to 100 mL.

Acetonitrile solutions

10% and 50% acetonitrile solutions were prepared in 0.1 M sodium perchlorate.

Potentiometric titration method

The potentiometric titration was carried out in divided cell. The electrical contact between two compartments was made by salt bridge filled with saturated solution of potassium chloride. Both ends of salt bridge were terminated with the help of glass wool and agar.

The potentiometer was calibrated prior to all sets of experiments. The indicator electrode (platinum) was cleaned by immersing in nitric acid prior to each experiment. The electrodes were thoroughly washed with distilled water, the platinum electrode was introduced in the solution to be titrated, and silver/silver chloride reference electrode was immersed in the saturated solution of potassium chloride. For each titration, 9-20 mg of 0.008 N 4-hydroxybiphenyl solutions was taken in a 100 mL beaker, respectively. Initial reading was noted. N-bromosuccinimide solution, 0.02 N, was added from burette in amounts of 0.5 mL. The solution was manually stirred during the titration. Volume of standard 0.02 N N-bromosuccinimide titrant added and the reading on e.m.f. scale after each addition was recorded. The end point was marked by the permanent yellow color when excess titrant (N-bromosuccinimide) was present.

For acetonitrile, the potentiometric titration was carried out in undivided cell, using Ag wire as reference electrode.

Calculations

4-Hydroxybiphenyl contents (mg) = NVE

where

N = Normality of N-bromosuccinimide

V = Volume of N-bromosuccinimide consumed

E = Equivalent weight of 4-hydroxybiphenyl (85 mg).

Conclusions

The results of present study indicate that 4-hydroxybiphenyl dissolved in mixed solvent system can be determined with N-bromosuccinimide potentiometrically. The property of N-bromosuccinimide to oxidize 4-hydroxybiphenyl has been used to estimate this compound. It readily and quantitatively oxidizes 4-hydroxybiphenyl and N-bromosuccinimide is reduced irreversibly to succinimide. The results of present study indicate that the height (cm) increases linearly with the increase in concentration of 4-hydroxybiphenyl determined. However, after 4-hydroxybiphenyl 30 mg, the results obtained are not reliable.

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