

NOTE

Hexacyanoferrate(III) as an Oxidant for the Titrimetric Determination of Benzoyl Hydrazine

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In the present note, the authors report the results of titrimetric determination of benzoyl hydrazine with hexacyanoferrate(III) in alkaline medium.

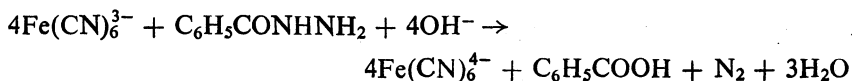
Benzoyl hydrazine belongs to a group of aroyl hydrazines that find extensive applications in chemotherapy, agriculture, industry and chemical analysis. The $-\text{NH}\cdot\text{NH}_2$ group of aroyl hydrazines is susceptible for oxidation by a number of oxidants¹⁻⁵. Similar methods for the determination of benzoyl hydrazine are scarce. A potentiometric method has been reported by Vulterin⁶ for the standardization of benzoyl hydrazine with potassium bromate. The direct determination of benzoyl hydrazine with hexacyanoferrate(III) has not been reported. In this communication, we report the results of the titrimetric determination of benzoyl hydrazine with hexacyanoferrate(III) in alkaline medium. Both potentiometric and visual indicator methods have been employed for the location of equivalence point.

A 0.1 N solution of hexacyanoferrate(III) was prepared and standardised. A 0.025 M solution of benzoyl hydrazine was prepared by dissolving Fluka's pure sample in deionised water and standardised against a standard solution of potassium bromate⁶. A 0.1% solution of osmium tetroxide (Johnson Matthey's, London) was prepared and stored in an amber coloured glass bottle. All other reagents were of AnalaR grade. A Toshniwal digital pH meter (CL 44) in combination with platinum and calomel electrodes was used in the potentiometric titration.

Preliminary experiments on the titration of BH with potassium hexacyanoferrate(III) using N-phenylanthranilic acid as indicator have shown that the end point is not found to be as sharp as that when potassium hexacyanoferrate(III) is taken as a titrant. Hence, subsequent studies were carried out taking BH as titrant in which the colour change is found to be sharp. It was also observed that the potentials at the platinum electrode during the electrometric titration of BH with hexacyanoferrate fluctuate and were stabilised in the presence of traces of osmium tetroxide. Moreover, the reaction becomes faster in presence of the reagent. Hence in all experiments, the oxidimetric titration was carried out in presence of this reagent which acts as a catalyst.

The variation of alkali on the titration of BH indicates that alkalinity below 1.0 M is not sufficient for the oxidation with hexacyanoferrate(III). The oxidation was found to be quantitative in the alkalinity range of 1.25 to 2.25 M at the beginning of titration. The effect of osmium tetroxide on the titration shows that 0.4 to 1.0 ml of 0.1% catalyst solution was adequate for the complete oxidation of BH in the alkalinity range of 1.25 to 2.25 M. Excess concentration of catalysts, however, is found to affect the sharpness in the visual detection of the end point.

In alkaline medium, hexacyanoferrate(III) generally undergoes one electron change with a redox potential of 0.45 V. It is found that four moles of oxidant are required for one mole of benzoyl hydrazine.



An aliquot of standard hexacyanoferrate(III) (containing from about 0.1992 to 0.3980 mmoles) is taken in a 250 ml conical flask and is treated with 6 M sodium hydroxide to give an alkalinity of 1.25–2.25 M, at the start of the titration followed by the addition of 0.5 ml and titrated with the test sample of benzoyl hydrazine solution using few drops of N-phenylanthranilic acid. The colour change at the end point is from yellowish brown to light green. The test sample to be analysed is dissolved and made up to the mark in an appropriate flask to give a solution corresponding to 0.025 to 0.030 M. The total amount of benzoyl hydrazine in 50 ml is calculated from the volume of benzoyl hydrazine consumed for known amount of hexacyanoferrate(III). The results are presented in Table 1.

TABLE I
RESULTS ON THE DIRECT DETERMINATION OF BENZOYL HYDRAZINE
WITH HEXACYANOFERRATE(III)

Sl. No.	Visual titration [Benzoyl hydrazine (mmoles)]			Potentiometric titration [Benzoyl hydrazine (mmoles)]		
	Taken	Found	% relative error	Taken	Found	% relative error
1.	0.1992	0.1984	+0.40	0.1992	0.1986	+0.30
2.	0.2490	0.2495	-0.20	0.2490	0.2488	+0.08
3.	0.2988	0.2981	+0.23	0.2988	0.2994	-0.20
4.	0.3486	0.3486	+0.00	0.3486	0.3481	+0.14
5.	0.3984	0.3992	-0.20	0.3984	0.3971	+0.32

In order to develop an accurate and rapid potentiometric procedure for the determination of benzoyl hydrazine and also to see whether there

is an indicator correction involved in visual titration outlined earlier, the authors have carried out the titration of hexacyanoferrate(III) with benzoyl hydrazine potentiometrically. The optimum concentration of catalysts and alkali concentration were found to be same as those obtained in the visual titration procedure. It was observed that the potential break at the equivalence point was about 120–150 m volts per drop (0.0 μ ml) of 0.025 M benzoyl hydrazine solution. Typical results are indicated in Table 1.

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(Received: 21 March 1990; Accepted: 4 April 1991)

AJC-283

ICHAC-3

THIRD INTERNATIONAL CONFERENCE ON HETEROATOM CHEM.

June 6–11, 1992

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