BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (7), 2155—2156 (1979)

Determination of Alkyl Thioureas, Isothiocyanates and Amines with Iodine Monochloride

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(Received August 26, 1978)

Iodine monochloride oxidizes thioureas to respective urea and sulfate in hydrogencarbonate medium. The iodine formed in the reaction is titrated with iodine trichloride to an Andrews end-point. This method has been applied to determine isothiocyanates and amines by their conversion to thioureas.

Most of the available procedures for determining thioureas by its oxidation to urea and sulfate require long standing periods in the range 5—60 min.[1-4]

A rapid and precise titrimetric method is described which requires a reaction period of about 30 s. Thioureas are reacted with iodine monochloride in hydrogencarbonate medium and the iodine formed is titrated with iodine trichloride to an Andrews end-point. This method does not require any blank determination and is unaffected by the presence of a number of concomitant substances.

This method of determining thioureas has been applied to analyze alkyl isothiocyanates involving conversion to substituted thiourea by reaction with 1-butylamine followed by oxidation with iodine monochloride. The present method has the advantage that basic or acidic impurities do not affect the results and that acid anhydrides and aldehydes, which interfere in acidimetric determination of isothiocyanates[5] by consuming amine *via* acylation and Schiff base formation respectively, can be tolerated. If the present method is coupled with acidimetry, the analysis of mixtures of isothiocyanates with isocyanates is possible since substituted ureas, formed by isocyanates, do not react with iodine monochloride.

The remarkable inertness of isothiocyanates towards several oxidizing agents, including iodine monochloride,[6] has added one more application. Primary and secondary amines react with an excess of 1-butylisothiocyanate and the substituted thiourea formed is again determined. Tertiary amines do not interfere.

Experimental

Reagents. Iodine monochloride[7] and iodine trichloride[8] solution, 0.1 mol dm^{-3} and 0.02 mol dm^{-3} respectively, were prepared in dilute hydrochloric acid and standardized iodometrically.[7]

Solutions of 1-butylamine, *ca.* 0.1 mol dm^{-3} and 1-butylisothiocyanate, *ca.* 0.1 mol dm^{-3} in dimethylformamide were used.

Test Compounds. All thioureas and amines were commercially available samples. Alkyl isothiocyanates were prepared and purified by the author.[9]

As a check independent methods were used to determine the purity of thioureas (Table 1). Solutions of amines and isothiocyanates, were prepared in dimethylformamide and the former were standardized by acidimetry[10] and the latter by the method of Vinson.[11]

Procedures. *Procedure for Thioureas*: Weigh or take an aqueous aliquot of sample containing 0.01—0.1 mmol of thiourea and dissolve or mix with 30 cm^3 of water, 2 g of sodium hydrogencarbonate and 10 cm^3 of carbon tetrachloride in a 250-cm^3 iodine flask. Introduce with swirling, 5—15 cm^3 of 0.1 mol dm^{-3} iodine monochloride, the excess being indicated by the appearance of iodine in organic layer. After swirling for 30 s, add cautiously 40 cm^3 of 6 mol dm^{-3} hydrochloric acid. When the evolution of carbon dioxide ceases, stopper the flask and shake vigorously. Titrate the liberated iodine by running in 0.02 mol dm^{-3} iodine trichloride until the solution becomes pale brown. Stopper the flask and shake well. Continue the addition of iodine trichloride in small portions, shaking vigorously after each addition, until the organic layer loses the last trace of violet color of iodine and becomes essentially colorless.

For a convenient and sharp end-point detection, invert the well-shaken-stoppered-flask and note the change from violet to colorless through the column of carbon tetrachloride at the neck of the flask.

Procedure for Isothiocyanates: Take a sample solution (5—10 cm^3) in dimethylformamide containing 0.01—0.1 mmol of isothiocyanate in a 250-cm^3 iodine flask and treat with 5 cm^3

TABLE 1. DETERMINATION OF THIOUREAS WITH IODINE MONOCHLORIDE

Thiourea, substituent	Purity, %				
	Present method	No. of detns.	Std. devn.	Comparison method	
—	99.9	8	0.08	99.8	Hypoiodite[4]
Methyl	99.7	10	0.10	99.9	Hexacyanoferrate (III)[12]
Allyl	99.5	6	0.10	99.2	Ce(IV) titration[13]
N,*N*′-Dimethyl	98.8	7	0.13	98.5	Bromine chloride[14]
Ethyl	98.5	6	0.09	98.7	Iodine[1]
N,*N*′-Diethyl	99.1	8	0.15	99.0	Iodine trichloride[15]
2-Propyl	99.0	6	0.12	99.3	Bromine[1]
1-Butyl	98.7	8	0.16	98.6	Bromine chloride[14]
2-Methyl-1-propyl	98.1	10	0.11	98.4	Ce(IV) titration[13]

of 0.1 mol dm^{-3} 1-butylamine. Swirl the solution and let stand for 10 min. Thereafter, add 30 cm^3 of water and determine the thiourea as before.

Procedure for Primary and Secondary Amines. Treat 5—10 cm^3 of sample solution in dimethylformamide containing 0.01—0.1 mmol of amine, with 5 cm^3 of 0.1 mol dm^{-3} 1-butylisothiocyanate in a 250-cm^3 iodine flask and age for 10 min. Dilute the contents with 30 cm^3 of water and determine the thiourea formed.

Results and Discussion

The iodine monochloride reacts with thiourea and its alkyl derivatives as follows:

$$\text{RNHCSNHR} + 8\text{ICl} + 5\text{H}_2\text{O} \longrightarrow \text{RNHCONHR} + 4\text{I}_2 + \text{H}_2\text{SO}_4 + 8\text{HCl}.$$

The reaction is slow in acid medium (20—30 min) but almost instantaneous and quantitative in the presence of hydrogencarbonate (Table 1). The concentration of hydrogencarbonate is not critical but it should be enough to neutralize the acid added with the reagent solution and that produced in the reaction. Iodine reacts with iodine trichloride as follows:

$$\text{I}_2 + \text{ICl}_3 \longrightarrow 3\text{ICl}.$$

The analysis of thiourea is utilized as a basis for the determination of isothiocyanate or amine if one of them is made to react with an excess of the other (Table 2):

$$\text{RNCS} + \text{RNH}_2 \longrightarrow \text{RNHCSNHR}.$$

TABLE 2. DETERMINATION OF ISOTHIOCYANATES AND AMINES

Substance	Range determined (mg)	No. of detns.	Average % recovery	Standard deviation
Isothiocyanate				
Ethyl	0.89— 8.65	8	100.2	0.3
Propyl	1.08—10.10	6	99.8	0.2
1-Butyl	1.30—11.00	8	99.9	0.1
2-Propyl	1.45—10.28	7	98.9	0.3
2-Methyl-1-propyl	1.25— 9.65	9	99.3	0.2
Allyl	0.99— 8.29	10	99.8	0.2
Amine				
Methyl	0.42— 3.08	6	99.9	0.2
Ethyl	0.45— 4.20	6	100.1	0.1
2-Propyl	0.62— 5.46	8	99.6	0.2
1-Butyl	0.87— 6.29	10	99.8	0.1
Diethyl	0.83— 6.07	6	99.7	0.3
Piperidine	0.89— 8.46	8	99.6	0.3

Mixtures of tertiary amines with primary or secondary amines can be analyzed if the total amine is known by acidimetry.$^{10)}$ Then, tertiary amine can be obtained by subtracting the amine found by iodine monochloride method. Mixtures of isothiocyanates with isocyanates can be analyzed if a total of them is determined by the method of Vinson,$^{11)}$ the isothiocyanate being known by the present method.

Iodine monochloride does not react with the following substances under the conditions of determination: citric acid, oxalic acid, glucose, glycine, alanine, arabinose, serine, diphenyldisulfide, carbon disulfide, formaldehyde, and benzaldehyde. Unsaturated compounds like allyl alcohol, cinnamic, and fumaric acids, that form addition compound with iodine monochloride, also do not interfere since the final titration involves determination of the liberated iodine.

Iodide, sulfide, sulfocyanide and thiosulfate interfere severely. Arylthioureas only reacted incompletely, therefore, the present method is not recommended for them.

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