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ALS (ACIDIC LITHIUM SULPHATE) DECOMPOSITION METHOD (PART IV)* KJELDAHL DETERMINATION OF NITROGEN IN HETEROCYCLIC RING COMPOUNDS CONTAINING NITROGEN–NITROGEN BOND

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Summary—Heterocyclic ring compounds containing nitrogen–nitrogen bonds such as 1H–1,2,4 triazole, 2,4,6 trimethylbenzenesulfonyltriazolide and pyridazine can be completely decomposed in the molten state with mixtures of various ratios of concentrated sulphuric acid and lithium sulphate (molten ALS) flux containing a catalyst such as silver sulphate. The quantitative recovery of nitrogen in the above three compounds with the molten ALS flux decomposition systems can be obtained by the Kjeldahl method.

One of the most widely utilized methods for the determination of nitrogen in various organic compounds is the Kjeldahl method[4,5] which has many merits such as a simple apparatus and the capability to treat many samples. But, the conventional Kjeldahl method suffers the disadvantage that complete recovery of nitrogen cannot be obtained from certain organic compounds.[5,6]

It is not possible to quantitatively determine nitrogen in organic compounds that contain azo, diazo, nitro, nitroso, oxime, hydrazine groups and heterocyclic ring compounds with the conventional Kjeldahl method. The compounds with the first six groups can of course be converted into amino compounds with catalysts such as Zn–Fe powder in hydrochloric acid media, and then a Kjeldahl determination of nitrogen is possible.[6] High temperature[4,5] and catalysts[7–13] are effectively utilized in the Kjeldahl decomposition.

Previous studies[2,3] have shown that the compounds with the groups of azo, diazo, nitro, nitroso, oxime, hydrazine and heterocyclic ring without N–N bonds can be rapidly decomposed and easily converted quantitatively to ammonia by use of molten acidic lithium sulphate (ALS) flux containing catalysts. Heterocyclic ring compounds containing N–N bonds are among the most difficult to obtain quantitative recovery of nitrogen with the conventional Kjeldahl method.[5,6] This paper demonstrates the quantitative decomposition of heterocyclic ring compounds containing N–N bonds such as 1H–1,2,4 triazole, 2,4,6 trimethylbenzenesulfonyl triazolide and pyridazine in the molten ALS flux containing a catalyst such as silver sulphate.

EXPERIMENTAL

Reagents

Boric acid, cupric sulphate, lithium sulphate monohydrate, sodium hydroxide, hydrochloric acid, concentrated sulphuric acid, elemental selenium powder, mercury(II) oxide(red), mercuric sulphate, silver sulphate, bromocresol green and methyl red were Wako Pure Chemical Co., analytical grade.

All other reagents were also of analytical grade. Demineralized distilled water was used throughout.

Samples of heterocyclic ring compounds containing nitrogen–nitrogen bond

1H–1,2,4 triazole, 2,4,6 trimethylbenzenesulfonyl triazolide and pyridazine were from Aldrich Chemical Co. and were analytical grade.

Apparatus

The Kjeldahl distillation apparatus used of the Parnas–Wagner type of Sibata Scientific Technology Ltd.

Decomposition procedures

Decomposition of heterocyclic ring compounds containing nitrogen–nitrogen bond with molten

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*Parts I, II and III are Refs 1, 2 and 3.

ALS flux. Weigh out 7.0 g of $Li_2SO_4 . H_2O$ and transfer to a dry 50-ml Kjeldahl flask. Accurately weigh approximately 10–100 mg of sample such as 1H–1,2,4 triazole or 2,4,6 trimethylbenzenesulfonyl-triazolide and transfer into the flask with a catalyst such as silver sulphate of 3.0 g. Add 3.0 ml of concentrated sulphuric acid and 5 ml of water to the flask in such a way that any solid in the neck is washed down. Place a small short-stemmed funnel in the neck of the flask and heat the flask with a Bunsen burner in a well-ventilated fume-hood, with the flask at 45° from the vertical. Heat with a small flame for about 20 min until the water has evaporated slowly.

When the water in flask has been removed and the contents have melted, increase the heat and continue the heating for about 30 min. At the end of the decomposition step, heat strongly for 10 min. After removal of the heat and before the molten ALS flux has cooled and solidified, add 30 ml of concentrated sulphuric acid and swirl gently. After cooling to room temperature with tap water, transfer the contents into a 50 ml volumetric flask and dilute to the mark with concentrated sulphuric acid. An aliquot of this sample solution is analysed by the Kjeldahl method for nitrogen.

Decomposition of pyridazine with molten ALS flux

After accurately weighing 2.1400 g of pyridazine, transfer to a 100-ml standard flask and dilute to the mark with water. Take out 5.0 ml of the pyridazine solution and transfer to the Kjeldahl flask. Weigh 7.0 g of $Li_2SO_4 . H_2O$ and transfer to a dry 50-ml flask. Add 3.0 g of catalyst, such as silver sulphate, and 3.0 ml of concentrated sulphuric acid to the flask. Decompose the samples and dilute to 50 ml with concentrated sulphuric acid as described previously.

Kjeldahl determination of nitrogen

Take 5.0–10.0 ml portions (accurately measured) of the sample solutions and transfer into a 100 ml beaker. Dilute to 10–20 ml with water and cool to room temperature with tap water.

Transfer to the Kjeldahl distillation apparatus. Generate ammonia with sodium hydroxide solution and absorb the ammonia in 30 ml of saturated boric acid solution. Continue the steam distillation until about 100 ml of liquid has distilled. Add a few drops of indicator (dissolved Bromocresol Green, 0.075%, and Methyl Red, 0.05%, in ethanol) to the ammonia absorption medium and titrate the $(NH_4)_2B_4O_{17}$ solution with standard 0.1*M* hydrochloric acid, using a 1-ml microburette. To find the right colour, it helps to have a comparison flask which contains 30 ml of saturated boric acid solution, 70 ml of distilled water and a few drops of the indicator. This will give a slight pink colour which is useful for noting when the colour change has occurred.

RESULTS AND DISCUSSION

Compounds with nitrogen present in a heterocyclic ring, such as pyrazine, pyrimidine, purine, quinoxaline, quinazoline, phthalazine, 1H–1,2,4 triazole, 2,4,6 trimethylbenzenesulfonyl triazolide and pyridazine are among the most difficult to rapidly decompose and quantitatively convert to ammonia with the conventional Kjeldahl method.[5,6] In particular, five or six membered heterocyclic ring compounds containing N–N bonds such as 1H–1,2,4 triazole and pyridazine are among the most difficult from which to quantitatively recover nitrogen from Kjeldahl method because the N–N bond of the ring compounds cannot be subjected to quantitative decomposition.

If a molten ALS flux without catalysts or with catalysts such as elemental selenium powder, selenium dioxide, cupric sulphate, mercuric sulphate or mercury oxide (red) is used, the heterocyclic ring compounds without N–N bonds such as pyrazine, pyrimidine, purine, quinoxaline and quinazoline can be decomposed and the nitrogen content can be quantitatively determined.[3] But the ALS decomposition method for determining N–N groups in 1H–1,2,4 triazole, 2,4,6 trimethylbenzenesulfonyl triazolide or pyridazine without catalysts or with catalysts such as elemental selenium powder, stannous sulphate, cupric sulphate, mercuric sulphate or mercury oxide (red) cannot be successfully employed (Runs 1–4 in Table 1) in contrast to phthalazine which can be quantitatively recovered with catalysts such as mercuric sulphate or mercury oxide (red).[3] However, if a molten ALS flux with a catalyst such as silver sulphate powder is used, these heterocyclic ring compounds containing N–N bonds can be readily decomposed and the nitrogen content quantitatively determined.

Table 1. Determination of nitrogen in five and six membered heterocyclic ring compounds

Samples	Additional reagents (*g*)*	Samples taken (*mg*)	Nitrogen (*mg*)	Found (%)	Decomposition time (*min*)	Run
1H–1,2,4 Triazole	$CuSO_4$ (1 g)[b]	10.4	3.14	30.2 (*n* = 1)†	60	1
(nitrogen content, 60.8%)	$SnSO_4$ (1 g)[b]	10.4	5.10	49.0 (*n* = 1)†	60	2
	HgO (1 g)[b]	59.5	17.4	29.2 (*n* = 1)†	60	3
	Elemental Se (0.1 g)[b]	10.4	0.86	8.27 (*n* = 1)†	60	4
	Ag_2SO_4 (2 g)[b]	26.0	15.3	58.8 (*n* = 2)	60	5
	Ag_2SO_4 (2 g)[b]	52.0	29.4	56.5 (*n* = 1)†	60	6
	Ag_2SO_4 (1 g)[a]	26.0	15.1	58.1 (*n* = 2)	60	7
	Ag_2SO_4 (2 g)[a]	26.0	15.6	60.0 (*n* = 2)	60	8
	Ag_2SO_4 (3 g)[b]	45.4	26.7	58.8 (*n* = 2)	60	9
	Ag_2SO_4 (3 g)[b]	97.6	54.7	56.0 (*n* = 1)†	30	10
	Ag_2SO_4 (3 g)[b]	104.2	60.5	58.1 (*n* = 1)	40	11
	Ag_2SO_4 (3 g)[b]	104.8	61.8	59.0 (*n* = 2)	60	12
	Ag_2SO_4 (3 g)[c]	103.9	57.7	55.5 (*n* = 1)†	60	13
				(Average 58.8%, S.D. 0.70)		
2,4,6 Trimethylbenzene-sulfonyl triazolide	Ag_2SO_4 (3 g)[b]	50.0	8.25	16.5 (*n* = 1)	60	14
(nitrogen content, 16.7%)	Ag_2SO_4 (3 g)[b]	79.8	12.9	16.2 (*n* = 2)	60	15
	Ag_2SO_4 (3 g)[b]	85.3	13.9	16.3 (*n* = 2)	60	16
	Ag_2SO_4 (3 g)[b]	107.8	17.2	16.0 (*n* = 1)	60	17
	Ag_2SO_4 (3 g)[b]	122.2	19.9	16.3 (*n* = 2)	60	18
				(Average 16.3%, S.D. 0.18)		
Pyridazine	Ag_2SO_4 (2 g)[a]	107.0	37.0	34.6 (*n* = 2)	60	19
(nitrogen content, 35.0%)	Ag_2SO_4 (2 g)[b]	107.0	36.3	33.9 (*n* = 2)†	60	20
	Ag_2SO_4 (2 g)[b]	107.0	35.9	33.6 (*n* = 2)†	60	21
	Ag_2SO_4 (3 g)[b]	107.0	37.0	34.6 (*n* = 2)	50	22
	Ag_2SO_4 (3 g)[b]	107.0	37.8	35.3 (*n* = 2)	60	23
	Ag_2SO_4 (3 g)[b]	107.0	38.4	35.9 (*n* = 2)	60	24
	Ag_2SO_4 (3 g)[b]	107.0	37.4	35.0 (*n* = 1)	60	25
				(Average 35.1%, S.D. 0.78)		

*Molten ALS flux [a]: from H_2SO_4–$Li_2SO_4 . H_2O$, 2.5 ml/7 g. [b]: from H_2SO_4–$Li_2SO_4 . H_2O$, 3.0 ml/7 g. [c]: from H_2SO_4–$Li_2SO_4 . H_2O$, 3.5 ml/7 g.

†Did not account for the values of average and standard deviation.

Decomposition of 1H–1,2,4 triazole and 2,4,6 trimethylbenzenesulfonyl triazolide

Heterocyclic ring compounds containing N–N bonds such as 1H–1,2,4 triazole and 2,4,6 trimethylbenzenesulfonyl triazolide can be completely decomposed by heating with the ALS flux with a catalyst of silver sulphate, but the decomposition time is long, *e.g.* 40–60 min. The decomposition time of 30 min for 1H–1,2,4 triazole gave lower recovery of nitrogen (Run 10 in Table 1).

The complete decomposition of these heterocyclic ring compounds with the concentrated sulphuric acid, lithium sulphate monohydrate and silver sulphate (3.0 ml, 7.0 g, 3.0 g) mixture requires gentle heating with a small flame for long periods (about 20 min) for evaporation of water because the additional water and the coordination water of lithium sulphate gives rise to bubbles. Then continuing with gentle heating for about 30 min to take a clean melting ALS flux and to decompose a sample, followed by heating with a stronger flame for about 10 min. Furthermore, the ratio of H_2SO_4–$Li_2SO_4 . H_2O$–Ag_2SO_4 (ml/g/g) in mixtures for the molten ALS flux is important for complete decomposition of N–N bonds in the heterocyclic ring compounds. Decomposition with the molten ALS flux of H_2SO_4–$Li_2SO_4 . H_2O$–Ag_2SO_4 (2.5 ml/7.0 g/1–2 g) mixture gave quantitative recovery of nitrogen in 26.0 mg of 1H–1,2,4 triazole (Run 7 and 8 in Table 1) but gave low recovery of nitrogen in 100 mg of 1H–1,2,4 triazole. The ALS flux of H_2SO_4–$Li_2SO_4 . H_2O$–Ag_2SO_4 (3.0 ml/7.0 g/2.0 g) system gave quantitative recovery of nitrogen in 26.0 mg of 1H–1,2,4 triazole but gave low recovery of nitrogen in 52.0 mg of 1H–1,2,4 triazole (Run 6 in Table 1). The ALS flux of H_2SO_4–$Li_2SO_4 . H_2O$–Ag_2SO_4 (3.0 ml/7.0 g/3.0 g) system gave quantitative recovery of nitrogen in 26.0–104.8 mg of 1H–1,2,4 triazole and in 50.0–122.2 mg of 2,4,6 trimethylbenzenesulfonyl triazolide. The ALS flux of H_2SO_4–$Li_2SO_4 . H_2O$–Ag_2SO_4 (3.5 ml/7.0 g/3.0 g) system gave low recovery of nitrogen in 1H–1,2,4 triazole (Run 13 in Table 1). After the heterocyclic ring compounds are decomposed, concentrated sulphuric acid (about 30 ml) must be added to the hot molten ALS flux to avoid solidification because a solidified molten ALS flux cannot be rapidly dissolved with concentrated sulphuric acid at room temperature.

When the molten ALS flux is cool, transfer the contents into a 50-ml volumetric flask and dilute to the mark with concentrated sulphuric acid. If the molten ALS flux is diluted with water, the silver sulphate precipitate in the flask. After the aliquot of the sample solution is transferred to the Kjeldahl distillation apparatus, a little water must be added to the apparatus before addition of sodium hydroxide because of the vigorous reaction of the concentrated sulphuric acid and the sodium hydroxide solution. Alternatively, after the aliquot of the sample solution is diluted with water and cooled to room temperature with tap water, the solution is transferred to the Kjeldahl distillation apparatus.

Decomposition of pyridazine

Heterocyclic ring compounds containing N–N bonds such as pyridazine are among the most difficult to quantitatively recover nitrogen with the conventional Kjeldahl method. Pyridazine is liquid at room temperature (25°) and therefore, the compound is diluted with water. An aliquot of this aqueous pyridazine solution is decomposed by molten ALS flux as described previously. In analogy with 1H–1,2,4 triazole and other compounds, the ratio of H_2SO_4–$Li_2SO_4 . H_2O$–Ag_2SO_4 (ml/g/g) in mixtures for the molten ALS flux is important for complete decomposition of N–N bond in the pyridazine.

Decomposition with molten ALS flux of H_2SO_4–$Li_2SO_4 . H_2O$–Ag_2SO_4 (2.5 ml/7.0 g/2.0 g) or H_2SO_4–$Li_2SO_4 . H_2O$–Ag_2SO_4 (3.0 ml/7.0 g/3.0 g) systems gave quantitative recovery of nitrogen in 107.0 mg of pyridazine but the mixture H_2SO_4–$Li_2SO_4 . H_2O$–Ag_2SO_4 (3.0 ml/7.0 g/2.0 g) gave a lower recovery of nitrogen content in pyridazine (Run 20 and 21 in Table 1). The molten state of the ALS flux from H_2SO_4–$Li_2SO_4 . H_2O$–Ag_2SO_4 (3.0 ml/7.0 g/3.0 g) mixture is the better decomposition system for heterocyclic ring compounds containing N–N bond. A flux[7–14] is effectively utilized for the decomposition of many organic and inorganic compounds and refractory minerals, due to the high temperature of the molten material.

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