Decomposition of Pyridine Compounds with Strong Phosphoric Acid-Iodic Acid: Some Information Obtained By Mass Spectrometry

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In the previous investigations[1] on the determination of nitrogen in organic compounds by the strong phosphoric acid-iodic acid decomposition method, satisfactory results were obtained for analyses of ammonium salts, amines, azo-compounds, pyrroles, thiazoles, nitro and oxime compounds, etc., but pyridine compounds did not give any good results and the reason for this was uncertain. The present investigation was undertaken to discover the reason and to find out a clue for extending this new analytical method to pyridine compounds. Particularly, for analyses of gases produced by the decomposition of nitrogen compounds, a mass spectrometer was employed effectively.

Several nitrogen compounds were decomposed with a mixture of strong phosphoric acid and potassium iodate at various temperatures, gases produced were swept into a gas reservoir with a flow of carbon dioxide, and then the gases analyzed by the mass spectrometer. On the other hand the sum of volumes of molecular nitrogen and nitrous oxide[2] obtained by the above procedure were compared with the theoretical ones. These results are shown in Table I. An example of analysis of a mass spectrum is illustrated in Table II.

A standard mass spectrum of each gas component anticipated was, of course, previously taken. Since the peak of m/e 22 in a mass spectrum is a characteristic one for carbon dioxide and it does not appear in spectra of the other components, each peak height due to carbon dioxide was calculated from the standard spectrum of pure carbon dioxide and the observed peak height of m/e 22. These are shown in the column 3 of Table II. By deducting the peak heights of carbon dioxide thus calculated from the initially observed peak heights, respectively, peak heights Δ_1 which are due to the other components than carbon dioxide were obtained. As in the peak heights of Δ_1 the peak of m/e 30 is produced only by the presence of nitrous oxide, the peak heights due to nitrous oxide were calculated in a similar way and so on.

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[1] S. Ohashi, This Bulletin, **28**, 177, 537 (1955); **29**, 700 (1956).

[2] Cf. S. Ohashi, Y. Takayama, H. Higashidani and S. Taki, This Bulletin, **30**, 604 (1957).

TABLE I

COMPOSITION OF GASES IN THE GAS RESERVOIR

(mol. %)

10 ml. of strong phosphoric acid and 600 mg. of potassium iodate were used in each analysis. The final reaction temperatures were kept for eight min.

Compound	Sample taken	Final reaction temp.	Reservoir volume	CO_2	N_2O	N_2	O_2	(N_2+N_2O)	
	mg.	°C	ml.	%	%	%	%	found ml.	calcd. ml.
Isonicotinic acid	20	233	125	ca. 100	0	0	0	0	1.9_5
〃	〃	253	113	97.8	1.0_1	0.8_5	0.3_8	2.1_0	,,
〃	〃	275	125	97.5	0.7_8	0.8_0	0.9_7	1.9_8	,,
Poly-2-methyl-5-vinyl-pyridine	〃	233	113	ca. 100	0	0	0	0	2.0_6
〃	〃	260	113	98.2	0.4_4	0.1_7	0.4_1	1.8_2	,,
Polyacrylonitrile	28	233	125	97.4	1.5_3	1.2_5	0	3.4_8	3.4_7
Acetanilide	33	233	125	98.4	1.0_2	0.5_5	0	1.9_8	1.7_6
Urea	25	233	113	97.1	2.2_0	0.4_8	0	3.0_5	3.2_0
Ammonium Sulfate	15	233	125	95.6	1.6_0	2.8_0	0	5.5_0	5.4_5

TABLE II

ANALYSIS OF MASS SPECTRUM

Sample: Isonicotinic acid 20 mg.
Date: Oct. 25, 1956, No. 4.
Magnetic current: 0.25 amp.
Scanning voltage: 3550 V.

Final reaction temp.: 275±2°C
n-Butane m/e 43: 58.99
Ionic current: 12.5 μ amp.
Sample pressure: 44.53 μ Hg.

M/e	peak height found	CO_2	Δ_1	N_2O	Δ_2	O_2	Δ_3	N_2	Δ_4
14	5.4	0.9_2	4.4_8	1.9_6	2.5_2		2.5_2	2.2_4	0.2_5
16	236.6_7	240.7_1	-0.40_6	0.6_9	-4.7_5	0.3_3	-5.0_8		-5.0_8
18	0.8								0.8
22	36.8	36.8	0						0
28	260.5	242.9_9	17.5_1	1.7_2	15.7_9	0.9_2	14.8_7	14.8_7	0
30	5.0	0.5_5	4.4_5	4.4_5	0				0
32	15.8	0.6_8	15.1_2		15.1_2	15.1_2	0		0
44	2123.7	2117.3_5	6.3_6	11.1_7	-4.8_1				-4.8_1
46	8.9	8.7_9	0.1_7	0.0_2	0.0_9				0.0_9

As indicated in Table I it was disclosed that pyridine compounds such as isonicotinic acid and poly-2-methyl-5-vinyl-pyridine are decomposed almost completely by heating with strong phosphoric acid-iodic acid at the temperature over 253° or 260°C, but at the same time oxygen is liberated by the self-decomposition of iodic acid. On the other hand, it was also found that amine, ammonium salt, and nitrile are completely decomposed at the temperature of 233°C, while pyridine compounds are not attacked at all at the same temperature. From these results it may be suggested that nitrogen in amines, ammonium salts, etc. and nitrogen in pyridine compounds would be separately determined by controlling the decomposition temperature with strong phosphoric acid-iodic acid, if oxygen liberated from iodic acid could be removed by any suitable means in the case of analysis of pyridine compounds.

Full details will be reported elsewhere in the near future.

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