Existence of Nitrous Oxide in Gases Produced from Nitrogen Compounds Decomposed by the Strong Phosphoric Acid-Iodic Acid Method

By Shigeru OHASHI, Yuzi TAKAYAMA*, Hiroshi HIGASHIDANI and Sachiko TAKI

(Received February 16, 1957)

In the previous papers[1] one of the authors presented a new method for the determination of nitrogen in nitrogen compounds. The compounds such as amines and ammonium salts are decomposed by heating with a mixture of strong phosphoric acid and potassium iodate to liberate the nitrogen contained in them. By sending the liberated nitrogen with carbon dioxide into an azotometer filled with a concentrated solution of potassium hydroxide, the nitrogen can be determined gas-volumetrically.

In the first course of this investigation, the gases accumulated in the azotometer by the procedure described above were considered as molecular nitrogen. However, it was found that amounts of liberated iodine[2] by the above reactions always exceeded the theoretical ones which were

* Mitsubishi Rayon Co. Ltd., Tokyo.

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

2) For the experimental details, cf S. Ohashi, This Bulletin, **28**, 171 (1955).

TABLE I

IODINE LIBERATED BY THE DECOMPOSITION OF NITROGEN COMPOUNDS WITH STRONG PHOSPHORIC ACID IODIC ACID

Compound	Sample taken mg.	I_2 found mg.	I_2 calcd. as N_2 mg.	I_2 calcd. as N_2O mg.	N_2O %
Ammonium Sulfate	102.6	136.0	118.3	157.3	44.9
,,	102.6	134.1	118.3	157.3	39.8
,,	102.6	138.0	118.3	157.3	49.4
,,	205.2	263.6	236.6	316.0	33.7
Acetanilide	15.7	116.4	115.0	117.9	75.0
,,	17.8	132.6	130.4	133.8	80.5
,,	24.3	179.9	178.0	182.5	74.4
,,	29.0	212.8	212.4	218.0	57.9
Urea	22.6	69.2	57.3	76.4	61.7
,,	39.1	118.1	99.2	132.2	57.2
,,	51.5	155.1	129.6	172.8	56.2
,,	71.5	228.2	181.3	242.0	77.8
Glycine	19.5	64.7	59.3	65.8	90.4
,,	29.9	97.8	91.0	101.1	86.0
,,	32.5	106.8	98.9	110.0	86.1

Reaction temp. below 240°C

TABLE II

ANALYSES OF NITROGENOUS GASES BY MASS SPECTROMETER

Compound	Sample taken	Composition of gases				$N_2O/(N_2+N_2O)$
		CO_2	N_2	N_2O	O_2	
	mg.	%	%	%	%	%
Ammonium sulfate	15	95.6	2.8_0	1.6_0	0	36
Acetanilide	33	98.4	0.5_5	1.0_2	0	65
Urea	25	97.1	0.4_8	2.2_0		82

Reaction temp. 233°C

calculated on the assumption that the nitrogen in the sample would be changed into molecular nitrogen. The data obtained for several nitrogen compounds are shown in Table I. The discrepancy between the observed and the calculated amount of iodine may be due to the fact that the nitrogen in the samples has not been converted into molecular nitrogen alone, but partly changed into nitrous oxide. For example, if molecular nitrogen is produced from urea by the oxidation with iodic acid, 3 mol. of iodine will be liberated from 5 mol. of urea.

$$5CO(NH_2)_2+6HIO_3 = 5CO_2+13H_2O+5N_2+3I_2$$

And if nitrogen oxide is produced from it, 4 mol. of iodine will be liberated from 5 mol. of urea.

$$5CO(NH_2)_2+8HIO_3 = 5CO_2+14H_2O+5N_2O+4I_2$$

In Table I all the found values of iodine are between those calculated from the two equations mentioned above, respectively. It indicates that the nitrogen in the sample may be converted into both molecular nitrogen and nitrous oxide. The contents of nitrous oxide in the gases calculated from the amounts of liberated iodine are also shown in Table I.

Since the evidence described above is still an indirect one for the existence of nitrous oxide in the gases, then in order to obtain direct evidence, the gases, produced by the decomposition of some nitrogen compounds with the mixture of strong phosphoric acid and potassium iodate, were swept into a gas reservoir with a flow of carbon dioxide and analyzed by a mass spectrometer. Although both nitrous oxide and carbon dioxide indicate the peak of M/e 30 in their mass spectra, the peak height due to carbon dioxide was much less than the observed one. Thus the existence of nitrous oxide was verified and its contents in the gases were determined[3]. The results of the analyses for

3) Cf. Y. Takayama and S. Ohashi, This Bulletin, **30**. 606 (1957).

ammonium sulfate, urea, and acetanilide are shown in Table II. It is clear that the gases from these compounds contain both nitrogen molecule and nitrous oxide and the latter takes about 30 to 80 % of the total nitrogenous gases.

In connection with the above results, the present authors doubted whether gases produced from nitrogen compounds by the Dumas' method are truly nitrogen molecule or not. Therefore isonicotinic acid, 2-methyl-5-vinyl-pyridine polymer, and β-dimethylamino-acetaldehyde-dimethylacetal were decomposed by the normal Dumas' method, in which a flow rate of carbon dioxide was about 6.7 ml./mm., and the gases produced were analyzed by the mass spectrometer. Also in the case of the Dumas' method, the existence of nitrous oxide was pointed out, but its amount was much less than that in the case of the strong phosphoric acid-iodic acid decomposition method.

Full details will be published in the near future.

Department of Chemistry, Faculty of Science, Kanazawa University
Kanazawa