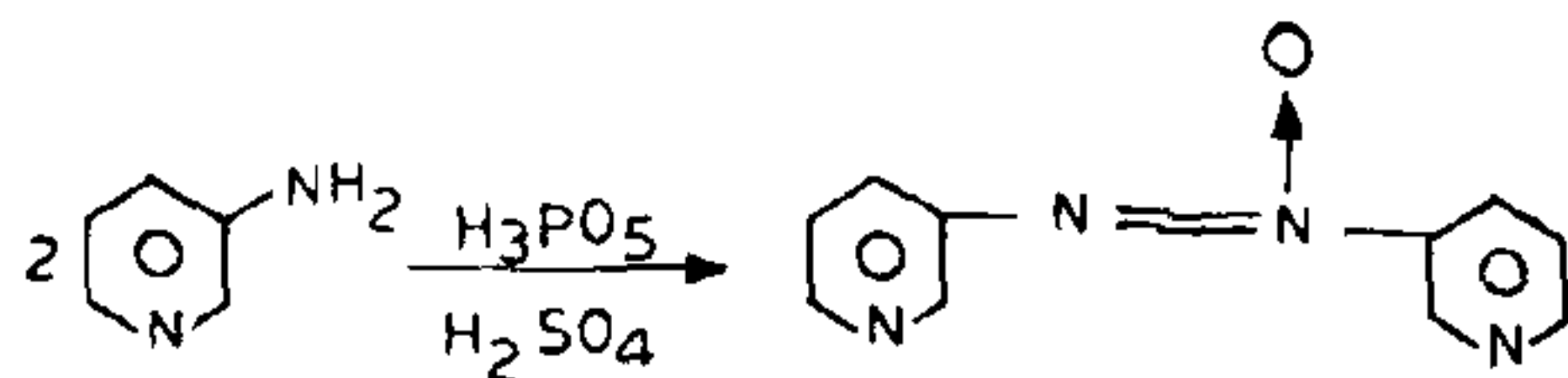


A NOVEL OXIDATION OF 3-AMINOPYRIDINE BY PEROXOMONOPHOSPHORIC ACID

RECENTLY Giam and Hauck¹ reinvestigated the Caro²'s acid oxidation of 3-aminopyridine and obtained 3-3'-azoxypyridine instead of 3-nitropyridine. The abnormal course of oxidation of 3-aminopyridine was recognised as early as 1951 by Hartman and Wiley³ in oxidation by H₂O₂-fuming sulphuric acid.

Our interest in the redox chemistry of peroxomonophosphoric acid PMPA prompted us to investigate the oxidation of 3-aminopyridine for the first time and we wish to report that 3-3' azoxypyridine is formed in well over 60% yields.



Experimental

Melting points were recorded on Thomas Hoover Capillary melting point apparatus and are not corrected. Elemental analysis were done by Michro-Tech. Laboratories, Skokie, Illinois. Potassium peroxodiphosphate was a gift from FMC corporation and was used as such. PMPA was prepared by the acid hydrolysis of peroxodiphosphate³.

3-3' azoxy pyridine

13.8 gm of potassium peroxodiphosphate (0.04 mole) was dissolved in 50 ml of water and 5 ml of cold conc. H₂SO₄ was added at the temperature of 10–12° C. 1 gm of 3-aminopyridine (Aldrich 99%) dissolved in 3 ml of conc. H₂SO₄ at 10–12° C was added to it and the reaction mixture was stirred for 4 hrs at room temperature. The mixture was cooled, neutralised with conc. NH₄OH and extracted with chloroform (5 × 50 ml), the extracts dried (MgSO₄), and rotary evaporated, leaving an orange solid (0.6 gms 60%). This was subjected to dry chromatography (50 gm) of silicagel and eluted with acetone which yielded an orange yellow solid. It was recrystallised from hot water to give yellow needles. m.p, 126° C lit. (127–128° C), M⁺ 200.

Analysis : Calc. for C₁₀H₈N₄O

C,	59.99	H,	4.03;	N,	27.99
Found C-	59.82	H-	4.09	N-	28.32

A kinetic study of the above reaction is in progress.

Department of Chemistry,
University of Illinois,
Chicago (USA),
and

S. N. MAHAPATRO.

Department of Chemistry,
Berhampur University,
Berhampur 760 007, India,
January 14, 1980.

G. P. PANIGRAHI,*
A. K. PANDA.

1. Giam, C. S. and Hauck, A. E., *Synthetic Communications*, 1978, 8 (2), 109.
2. Hartman, J. L. and Wiley, R. H., *J. Am. Chem. Soc.*, 1951, 73, 494.
3. Fortnum, D. H., Battaglia, C. J., Cohen, S. R. and Edwards, J. O., *Ibid.*, 1960, 82, 778.

1-HYDROXY-2-ACETONAPHTHONEOXIME AS A GRAVIMETRIC REAGENT FOR PALLADIUM(II), COPPER(II) AND NICKEL(II)

IN continuation of our earlier work on the analytical applications of 1-hydroxy-2-acetonaphthoneoxime^{1,2}, we now report its use as a gravimetric reagent. The reagent gives a deep yellow precipitate with palladium (pH 1.5–2.5), grey precipitate with copper (pH 3.5–6.0) and a greenish yellow precipitate with nickel (pH 8.0–10.0).

An aliquot of the standard³ palladium chloride solution was diluted to 100 ml with distilled water and the pH adjusted to about 1.5 with hydrochloric acid (2M). A 1% (W/V) alcoholic solution of the reagent was added to it. The precipitate was digested for 15 min, cooled, filtered, washed with aqueous alcohol (4 : 1), dried at 110–120° C and weighed. The gravimetric factor for palladium is 0.2099. Copper(II), nickel(II), aluminium(III), manganese(II), zinc(II), platinum(IV), ruthenium(III) and rhodium(III) did not interfere. The interference due to iron(III) was eliminated by masking with tartrate. Some results are shown in Table I.

Copper(II) was precipitated from the standard³ copper sulphate solution in presence of sodium acetate-acetic acid buffer (pH 4.5) following the procedure described above. The gravimetric factor for copper is 0.1370. Cadmium(II), nickel(II), zinc(II), chromium(III), manganese(II) did not interfere. The procedure developed was applied for the determination of copper in brass, gun-metal and chalcopyrites. Typical results are given in Table I.

Nickel(II) was similarly precipitated from the Standard³ nickel sulphate solution in presence of ammonium chloride-ammonia buffer (pH 8.5). The gravimetric factor for nickel is 0.1278. Copper(II), cadmium(II) and chromium(III) did not interfere. When iron(III) and aluminium(III) were present, tartrate was to be added. Cobalt(II) and manganese(II)

TABLE I
Determination of palladium, copper and nickel with 1-hydroxy-2-acetonaphthoneoxime.

Metal and alloy or ore	Computed value, mg	Experimental value, mg	Diff. mg.	Error %
1. Palladium	(DMG Method)			
(a) Stock solution	5.29	5.31	+0.02	+0.38
(b) Ternary mixture	10.57	10.63	+0.06	+0.57
2. Copper	(Iodometric Method)			
(a) Stock solution	10.02	10.04	+0.02	+0.20
(b) Brass	14.28	14.32	+0.04	+0.28
(c) Gun-metal	10.55	10.58	+0.03	+0.28
(d) Chalcopyrites	7.14	7.18	+0.04	+0.56
(e) Constantan	14.60	14.73	+0.13	+0.34
(f) German silver	12.16	12.14	-0.02	-0.16
(g) Ternary mixture	10.55	10.59	+0.04	+0.38
3. Nickel	(DMG method)			
(a) Stock solution	11.30	11.32	+0.02	+0.18
(b) Raney nickel	12.35	12.32	-0.03	-0.24
(c) Nichrome	12.07	12.11	+0.04	+0.33
(d) Constantan	12.48	12.42	-0.06	-0.48
(e) German silver	9.90	9.87	-0.03	-0.30
(f) Ternary mixture	11.30	11.25	-0.05	-0.44

interfered by giving brown and dark green precipitates respectively with the reagent. However, the interference due to cobalt(II) was overcome by the use of thiocyanate. The procedure developed was utilised for the determination of nickel in raney nickel and nichrome. The results are represented in Table I.

Determination of copper and nickel in a mixture of the two :

Copper was precipitated in the presence of sodium acetate-acetic acid buffer (pH 4.5), digested, filtered, washed, dried and weighed. The filtrate was concentrated to about 100 ml and nickel was precipitated in presence of ammonium chloride-ammonia buffer. The procedure was employed in the determination of copper and nickel in constantan and german silver. The results are given in Table I.

Determination of palladium, copper and nickel from the mixture.

Palladium was precipitate in the pH range 1.5-1.2.5 and filtered. The filtrate was concentrated, neutralised with NaOH, the pH adjusted to 4.5 and copper precipitated. The volume of the filtrate was reduced to about 100 ml and nickel was determined after adjusting the pH to 8.5. Typical values are given in Table I.

Determination of the error of the method:

Palladium (5.0-35.0 mg), copper (4.0-40.0 mg) and nickel (10.0-40.0 mg) were determined with an average

error of $\pm 0.22\%$, $\pm 0.21\%$ and $\pm 0.21\%$ respectively. Six determinations each of 10.57 mg of palladium, 10.02 mg of copper and 11.30 mg of nickel gave a standard deviation of 0.05₂, 0.02₃ and 0.02₃ mg respectively, the relative mean error being $\pm 0.19\%$, $\pm 0.16\%$ and $\pm 0.09\%$ respectively.

The literature survey indicates that 2-hydroxy-4-methoxy-5-methyl chalconoxime⁴ has also been used for the consecutive determination of palladium, copper and nickel. The results presented above are comparable to those obtained with that reagent.

One of the authors (VVB) is grateful to CSIR, New Delhi, for a research fellowship.

Department of Chemistry,
S.V. University,
Tirupati 517 502,
November 29, 1979.

V. V. BALAKRISHNA,
N. APPALA RAJU.

1. Prasada Rao, N. V. K. N., *M.Phil. Dissertation*, S.V. University, Tirupati, India, 1978.
2. Balakrishna, V. V. and Appala Raju, N., *Curr. Sci.*, 1979, 48, 724.
3. Vogel, A. I., *A Text-Book of Quantitative Inorganic Analysis*, 3rd edition, ELBS and Longman, London, 1975, pp. 512, 358 and 479.
4. Deshmukh, B. K., Vyas, C. N. and Kharat, R. B., *J. Indian Chem. Soc.*, 1975, 52, 385.