A Pd(II)-Cu(II) Catalyst for the Kjeldahl Analysis of Nitrogen in Pyridines

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Synopsis. A serious drawback of the Kjeldahl analysis of organic nitrogen, that pyridine derivatives were difficult to degrade to ammonia, was overcome by use of a Pd(II)–Cu(II) catalyst. Three hours of digestion at approximately 320 °C using the catalyst were found to be sufficient for quantitative liberation of ammonia from pyridines.

Nitrogen determination with the Kjeldahl method does not require expensive devices nor specialized techniques, and is precise and accurate.[1] Nevertheless, it has been almost ignored as a means of organic elemental analysis. One reason for this may be because of difficult degradation of pyridine derivatives to ammonia. Mixtures of mercury and selenium were used as catalysts for the degradation.[2–6] These required a long digestion period and were not widely used because of environmental concerns. Recently, the use of hydrogen peroxide as an oxidizing reagent was reported to greatly shorten the digestion period.[6–8] However, it does not seem easy nor safe to handle 50% hydrogen peroxide at high temperatures.

By analogy to the high reactivity of palladium(II) in organometallic chemistry such as the metallation of a phenyl ring,[9] we expected that Pd(II) could provide a means to break down an inert pyridine nucleus.

Experimental

Reagents. Amidosulfuric acid of standard grade for volumetric analysis, acetanilide of standard grade for elemental analysis, and other inorganic reagents of superior grade were purchased from Wako Pure Chemical Ind. 4,4′-Dimethyl-2,2′-bipyridine and other reagent grade organic materials were purchased from Aldrich Chemical Co. and Tokyo Kasei Kogyo Co., respectively. All chemicals were used as received.

Procedure. A standard procedure for a general micro-Kjeldahl method[1] was followed with some modifications. A 10—11 mg portion of sample was weighed into a digestion flask using a small glass boat. Five hundred milligrams of potassium sulfate, catalyst, and 2 ml of concentrated sulfuric acid were added to the flask. The digestion using an electric furnace (Model ME-6, Shibata Co.) was carried out with gentle refluxing of sulfuric acid at approximately 320 °C. After 6 min of distillation of ammonia from the alkalinized mixture into 5 ml of 2% aqueous boric acid containing Methyl Red-Bromocresol Green indicator, the green solution obtained was titrated with 0.01 mol dm^{-3} aqueous amidosulfuric acid to a blue color, which was the same color as a blank run.

Results and Discussion

Figure 1 shows the dependence of nitrogen content found in 4,4′-dimethyl-2,2′-bipyridine upon the degradation time in the case of 2 mg of $PdCl_2$ as a catalyst. Diverse results at 4 h of digestion seemed to depend on the sample position on the furnace; efficiencies of heating were slightly different from place to place among six locations for digestion flasks. Six hours of digestion assured a good reproducibility, but were too long considering the period needed for preparation, distillation, and titration; 3 h may be a practical time. We tried to use a second catalyst to activate palladium to shorten the period of digestion.

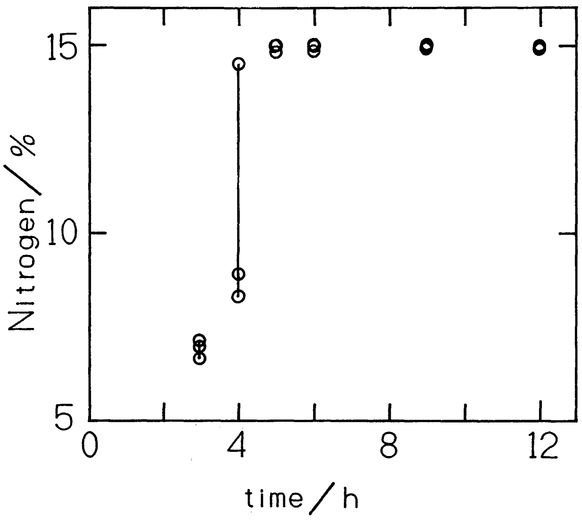

Fig. 1. Dependence of nitrogen content found for 4,4′-dimethyl-2,2′-bipyridine on the digestion time using 2 mg of $PdCl_2$ as a catalyst.

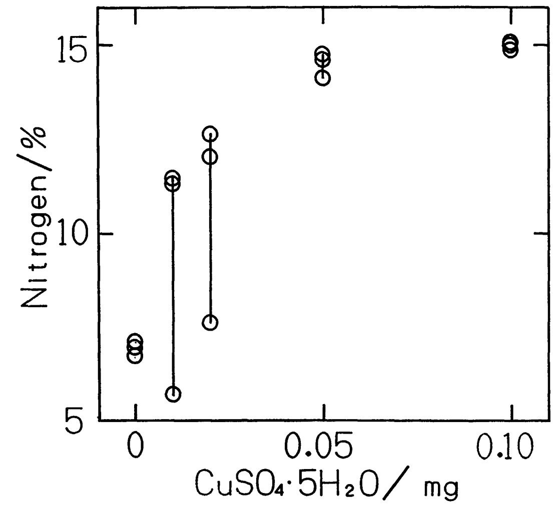

Fig. 2. Nitrogen content found for 4,4′-dimethyl-2,2′-bipyridine by digestion with 2 mg of $PdCl_2$ for 3 h using various amounts of $CuSO_4 \cdot 5H_2O$.

In the Wacker process, Pd(0), formed by the reaction of Pd(II) with ethylene to produce acetaldehyde, is oxidized to Pd(II) by oxygen with the mediation of a Cu(I)–Cu(II) redox pair.[10)] By analogy to this, the effects of $CuSO_4 \cdot 5H_2O$ were examined by digesting for 3 h using 2 mg of $PdCl_2$. A very small amount of Cu(II) was found to be effective as shown in Fig. 2.

Figure 3 shows the dependence of nitrogen content found at 3 h of digestion in the presence of 30 mg of $CuSO_4 \cdot 5H_2O$ upon the amount of $PdCl_2$. Even when a large amount of $CuSO_4 \cdot 5H_2O$ was used, a quantity of $PdCl_2$ larger than 1.5 mg was found to be necessary to attain complete liberation of ammonia.

As shown in Fig. 4, the 3 h digestion time could not be shortened even by using both 2 mg of $PdCl_2$ and 30 mg of $CuSO_4 \cdot 5H_2O$.

Several pyridine derivatives, tris(2,2′-bipyridine)iron(II) diperchlorate, and tris(2,2′-bipyridine)ruthenium(II) diperchlorate were analyzed for nitrogen under the conditions optimized above, namely, 3 h of digestion using 500 mg of K_2SO_4, 2 ml of H_2SO_4, and 30 mg of the Pd–Cu catalyst prepared previously by mixing 2 parts by weight of $PdCl_2$ with 30 parts by weight of $CuSO_4 \cdot 5H_2O$ using an agate mortar. In these experiments, three positions on the furnace were used for samples and the other three were used for reference acetanilide. Two flasks for blank runs were heated during the distillation of ammonia from the sample and reference. For reference acetanilide, we obtained 98.84±0.26% of ammonia, with a 95% confidence limit in 32 experiments, using the Pd–Cu catalyst. The difference from 100% was due to losses by manipulation. Values in Table 1 have been corrected for these losses by using values obtained in the reference runs which were carried out simultaneously. The effect of the Pd–Cu catalyst can be seen as significant. In the absence of the catalyst, no ammonia was liberated from pyridine ring. Interestingly, this appeared even in the cases of nicotinamide and cinchonine, where half of the nitrogen content could be detected, corresponding to the nitrogen of the carbamoyl group and the quinuclidine structure, respectively. In the presence of the catalyst, however, a quantitative amount of ammonia was generated, idicating complete degradation of the pyridine ring.

Although $[Ru(bpy)_3]^{2+}$ appeared to degrade by the appearance of digestion, no nitrogen was detected. The fact that the digestion of ammonium sulfate as a substrate in the presence of $RuCl_3 \cdot H_2O$ gave no ammonia in the distillate indicated that oxidation of ammonia to some volatile species was catalyzed by Ru. Platinum was also

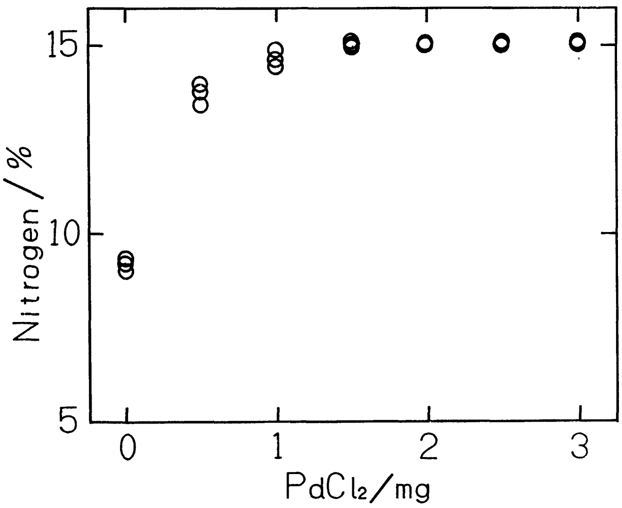

Fig. 3. Nitrogen content found for 4,4′-dimethyl-2,2′-bipyridine by digestion with 30 mg of $CuSO_4 \cdot 5H_2O$ for 3 h using various amounts of $PdCl_2$.

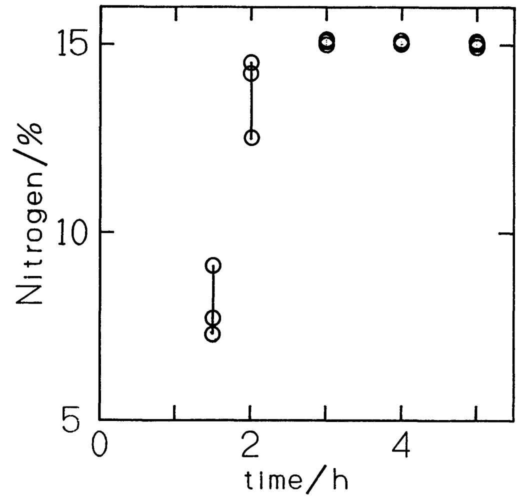

Fig. 4. Dependence of nitrogen content found for 4,4′-dimethyl-2,2′-bipyridine on the digestion time using 2 mg of $PdCl_2$ and 30 mg of $CuSO_4 \cdot 5H_2O$.

Table 1. Kjeldahl Analysis of Nitrogen in Pyridines with and without Use of the Pd–Cu Catalyst

Pyridine derivative	Formula	Nitrogen content/%		
		Calcd	Found	
			without	with
4,4′-Dimethyl-2,2′-bipyridine	$C_{12}H_{12}N_2$	15.20	0.80	15.16
2,2′-Bipyridine (bpy)	$C_{10}H_8N_2$	17.94	0.89	17.97
Acridine	$C_{13}H_9N$	7.82	0.67	7.86
Nicotinamide	$C_6H_6N_2O$	22.94	11.83	22.96
Cinchonine	$C_{19}H_{22}N_2O$	9.52	4.58	9.51
$Fe(bpy)_3(ClO_4)_2$	$FeC_{30}H_{24}N_6Cl_2O_8$	11.62	3.45	11.65
$Ru(bpy)_3(ClO_4)_2$	$RuC_{30}H_{24}N_6Cl_2O_8$	10.94	0.06	0

found to have this catalytic effect. Palladium selectively attacked a pyridine ring to liberate ammonia and did not oxidize ammonia further.

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