Novel Formation of Nitrate and Ammonium Ions by Reaction of Inorganic Molybdenum Nitride with Hydrogen Peroxide

Noritaka Mizuno,† Hitoshi Nakajima, Hitoshi Tanaka, and Tetsuichi Kudo
Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106
†Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Bunkyo-ku, Hongo, Tokyo 113

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A reaction of molybdenum nitride with hydrogen peroxide was characterized by elemental analysis, ^{14}N NMR, IR, XPS, TOF mass, and TG/DTA spectroscopy and acid/base, ammonia, and peroxo titration with NaOH, indophenol, and $KMnO_4$ reagents, respectively. It was found that nitrate and ammonium ions as well as peroxoisopolymolybdates were produced by the reaction.

Inorganic metal nitrides have attracted much attention in the fields of material science,[1-5] catalysis,[6-12] and so on, owing to their high stability to thermal and mechanical treatments and specific surface reactivity. So the investigation of the reactivity is interesting for the better understanding and precise control. However, almost nothing is known of the reactivity of inorganic metal nitrides having atomic nitrogen at interstitial position except that some nitrides are chemically quite inert or those do react tend to decompose and hydrolyze to give dinitrogen and ammonia, respectively. Nothing is known of the formation of nitrate ion.[1-3,13] In addition, the mineralization of organic nitrogen to ammonium ion and its subsequent oxidation to nitrate ion are the major bottlenecks restricting supply of the nutrient to plants.[14,15] In industry, the oxidation of ammonia to nitric acid needs three steps and the first step (oxidation of ammonia to nitrogen monoxide) is carried out above 800 °C.[16] Therefore, the formation of nitrate ion is also interesting on the standpoint of oxidation catalysis.

On the other hand, to date the reactivity of organometallic compounds of Mo with dinitrogen ligands have extensively been studied and ammonia, hydrazine, and dinitrogen have been identified as products.[17-21] However, almost nothing is known of formation of nitrate ion even for the reaction of these organometallic compounds.

In this report, we focused on the reactivity of inorganic nitride of molybdenum and found the novel reaction of inorganic molybdenum nitride with hydrogen peroxide to form nitrate and ammonium ions.

Nitride of Mo (High Purity Chemicals), 30% aqueous hydrogen peroxide (Junsei Chemical), 0.01 M aqueous NaOH, and 0.002 M aqueous $KMnO_4$ (Wako Pure Chemicals) were commercially obtained and used without further purification. It was confirmed that the structure of molybdenum nitride was cubic Mo_2N (with a trace amount of Mo metal) and that the atomic ratio of N/Mo was 0.50 and well agreed with the stoichiometric ratio of Mo_2N. The content of hydrogen in molybdenum nitride was $\leq 0.04\%$. These facts suggest that the content of ammonia in starting molybdenum nitride is very low. The molybdenum nitride was not dissolved with nitric acid but aqua regia in consistent with a literature.[13]

The reaction of molybdenum nitride with hydrogen peroxide was carried out as follows: Finely powdered solid molybdenum nitride (200 mesh; 2 g for molybdenum nitride (0.019 molar atomic Mo)) was added to an aqueous solution of hydrogen peroxide (15%). The solution was kept at room temperature for 24 h (final pH = 2.0). Then the solution was filtered to remove unreacted molybdenum nitride and Pt net was put into the solution to decompose excess hydrogen peroxide. The resulting solution was evaporated to dryness at 33±2 °C. Finally the solid was dried in vacuo at room temperature for 12 h. Hereafter, the resulting solid obtained from molybdenum nitride is abbreviated by (**I**). The yield of (**I**) was ca. 89% on Mo-basis.

Table 1. Data of elemental analysis, ^{14}N NMR, and titration

Element[a] / wt%			Ratio of NH_4^+ / NO_3^- [b]	Amount[c]/ wt%	
M	N	H		NH_3	O_2^{2-}
52	1.6	2.1	1.2	0.93	18.4

[a] Elemental analysis. [b] Integrated ^{14}N NMR signal intensity ratios. [c] Measured by titration with NaOH, indophenol, and $KMnO_4$ reagents, respectively.

Infrared spectra were measured as KCl pellets with a Perkin-Elmer Paragon1000 PC spectrometer. The ^{14}N NMR spectra of samples (solvent, D_2O; 27 °C) were recorded on JEOL-GX 270 FT spectrometer using liquid ammonia as a reference. X-ray photoelectron spectra were recorded for self-supporting discs with a JEOL JPS-90SX spectrometer using an Mg-Kα source (1253.6 eV). The binding energies were corrected by using the value of 285.0 eV for the C1s peak resulting from carbon contamination.

Contents of nitrogen and hydrogen were determined using a gas chromatographic CHN analyzer (Yanagimoto MT-3). The content of metal was determined with a ICP spectrometer (Shimadzu ICPS 2000). It was confirmed that the content of Mo in (**I**) was 52 wt% and in good agreement with 52 wt% obtained from the weight of MoO_3 formed by heating (**I**) up to 500 °C in air. The formation of MoO_3 was confirmed by XRD. Numbers of ammonia, peroxo group O_2^{2-}, and proton were quantitatively analyzed by using indophenol,[22] $KMnO_4$, and aqueous NaOH reagents, respectively.

Table 1 summarizes the data of elemental analysis and titration of NH_3 and O_2^{2-}. The elemental analysis found: N, 1.6; H, 2.1; Mo, 52.0 (wt%). This fact shows that nitrogen is included in (**I**). The NH_3 content measured by an indophenol reagent was 0.92 wt%. The N/Mo atomic ratio of (**I**) was 0.21 and decreased from 0.5 of starting molybdenum nitride. The formation of dinitrogen, of which the amount approximately corresponded to the difference, was observed by gc analysis.

Next, the state of nitrogen was investigated. Figures 1a and 1b show ^{14}N NMR spectra of samples prepared by the reaction of nitride of Mo and NH_4NO_3, respectively. NH_4NO_3 showed two peaks at 20.7 and 377.0 ppm with an intensity ratio of 1.0 :

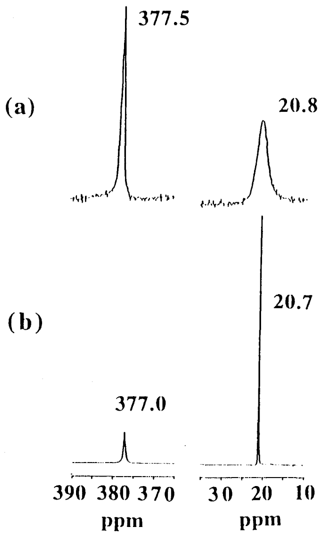

Figure 1. ^{14}N NMR spectra of (**I**) and ammonium nitrate. (a) (**I**) and (b) ammonium nitrate.

1.0, which are assignable to NH_4^+ and NO_3^-, respectively.[23] The spectrum of (**I**) (Figure 1a) showed two broad peaks at 20.8 ($\Delta\nu 1/2$, ca. 100 Hz) and 377.5 (35 Hz) ppm with an intensity ratio of 1.2 : 1, respectively. No signals due to N_2H_4 and NO_2^- were seen. In addition, the amount of NH_3 (0.76 wt% as N) obtained by the titration by using indophenol approximately agreed with that (0.87 wt% as N) calculated by {the content of N in (**I**)} x $\{I_{NH_4^+} / (I_{NH_4^+} + I_{NO_3^-})\}$, where $I_{NH_4^+}$ and $I_{NO_3^-}$ express the integrated ^{14}N signal intensities of NH_4^+ and NO_3^-, respectively. The agreement shows that the two peaks at 20.8 and 377.5 ppm include almost whole nitrogen atoms in (**I**).

The amounts of ammonia as well as the data of elemental analysis and NMR data of $I_{NH_4^+} / I_{NO_3^-}$ are shown in Table 1. The amounts of ammonia obtained by the titration are in close agreement with those calculated based on data of elemental analysis and NMR in the same way as those described above. The present results show that ammonium and nitrate ions are formed by the reactions of nitride of Mo with hydrogen peroxide. It was confirmed for (**I**) that IR and XPS results were consistent with NMR data: In the range of 1300 - 1600 cm^{-1}, the IR spectrum showed a 1402-cm^{-1} band and a 1324-cm^{-1} shoulder, which are assigned to $\delta(NH_4^+)$ and $\nu(NO_3^-)$, respectively.[24,25] X.p. spectrum of (**I**) in N1s region showed signals at 402.2 eV and 406.3 eV assigned to NH_4^+ and NO_3^-, respectively.[26] Thus, the elemental analysis, NH_3 titration, and IR and NMR spectroscopy show the formation of NO_3^- and NH_4^+ ions by the reaction of molybdenum nitride with hydrogen peroxide. The oxidation and reduction of nitrogen in molybdenum nitride is in contrast with the oxidation of carbon in tungsten carbide to form oxalate ion and carbon oxides.[27]

Next, the chemical formula of peroxoisopolymolybdate was investigated and that of the main species was estimated to be $H_8(NH_4)Mo_8O_{20}(O_2)_8(NO_3)(H_2O)_3$ on the basis of following data. The H^+/(**I**) ratio determined by a acid/base titration was 8. The number of water in (**I**) was determined to be 3.0 by TGA analysis. The positive TOF mass spectrum of (**I**) in the range of m/e 1000 - 5000 gave the most intense peak at 1486±5, which may correspond to $\{H_9(NH_4)Mo_8O_{20}(O_2)_8(NO_3)(H_2O)_3\}^+$. Subsequent loss of MoO_3 fragment is the other dominant feature and resulted in the peak at 1342. The formation of peroxooctamolybdate ion was also reported by Trysberg and Stomberg.[28] The large $\Delta\nu 1/2$ in Figure 1a and the fact that no signals due to NH_4NO_3 were observed by XRD suggest an interaction of NH_4^+ and NO_3^- ions with peroxoisopolymolybdate anion formed. X.p. spectrum of (**I**) in Mo3d region consist of an Mo3d3/2 and Mo3d5/2 doublet, 236.4 and 232.8 eV, respectively, in agreement with those reported for Mo^{6+}.

In conclusion, the present results show the novel formation of nitrate and ammonium ions by the reaction of metal nitrides with hydrogen peroxide.

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