

On the Existence of Bivalent Ions in the Apatite Channels: A New Example—Phosphocalcium Cyanamido-Apatite

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Received March 13, 1981; in revised form July 2, 1981

A new apatite, phosphocalcium cyanamido-apatite $\text{Ca}_{10}(\text{PO}_4)_6 \text{CN}_2$, is obtained by treatment under low pressure at high temperature (900–1000°C) of a mixture of the corresponding hydroxyapatite and calcium cyanamide. In this apatite, one CN_2^- ion associated with a vacancy replaces two hydroxyl ions in the channels. The formation of a cyanamide-containing apatite also occurs by treatment of an A-type carbonated apatite by ammonia at 600–900°C: in the latter case, the reaction seems more difficult and more limited than in the former. The cyanamido apatite is decomposed by heating in air, and it gives rise first to an A-type carbonated apatite, with release of both ammonia and nitrogen oxide and second to hydroxyapatite by hydrolysis of the A-type carbonated apatite.

Introduction

In the last decade, considerable attention has been paid to the formation and reactivity of apatites. The increasing effort in this field is due to the importance of apatitic compounds either in the study of calcified tissues or in the beneficiation of natural phosphates. So a better insight of apatites' crystallochemical properties has been obtained; and, besides, a lot of rather unusual new apatites have been discovered: these latter apatites refer to compounds in which unusual substitutions occur either on cationic or anionic sites of the lattice, with respect to the well-known calcium phosphate hydroxyapatite or fluorapatite. Some examples of such substitutions are:

(a) the XO_4^{3-} sites of apatites can be occupied by ReO_3^- (1)

(b) the cationic sites of lead apatites can be partially filled by NH_3^+ groups (2, 3). This substitution occurs when glycine in the form of zwitter ion, $\text{NH}_3^+ \text{CH}_2\text{COO}^-$ enters the apatitic lattice: the NH_3^+ part is located on a cationic site of the channel surrounding, while the anionic part lies in the channel.

(c) the hydroxyl sites (or channel sites) have been recently shown to be occupied either partially or completely by N^{3-} ions (4, 5): the balance charge is then compensated by the coupled substitution $\text{Ca}^{2+} \rightarrow \text{Me}^{3+}$.

Besides the presence of molecular oxygen has been first postulated by Simpson (6), and confirmed in our laboratory: our results show the simultaneous presence of oxygen in different oxidation states in the channels of oxygenated apatites (7–9).

Another unusual kind of substitution has been studied in great detail in our laboratory: it is relative to the replacement of two

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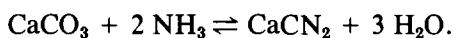
hydroxyl ions of hydroxyapatite (Hap) by a bivalent ion associated with a vacancy in order to maintain the balance charge. This kind of substitution has been the subject of many controversies all the last century: particularly the existence of so-called oxyapatites (Oxap) and A-type carbonated apatites (ACap)¹ has been claimed and then contradicted (10). However, in the last 30 years, evidence has been afforded for the formation in very special conditions of A Cap (11–15) or Oxap. (16–18).

Moreover, in the same time, other apatites containing bivalent ions associated with vacancies have been discovered: for instance, peroxyapatites (19, 20) or sulfide apatites (21). As will be discussed, the formation of such apatites can be understood by considering the very high reactivity of Oxap.

In this paper the formation of a new apatite, of the same kind, phosphocalcium cyanamido apatite (CN₂ap), Ca₁₀(PO₄)₆CN₂, will be discussed. The reactivity of this apatite will be considered as well.

Materials and Methods

The starting products hydroxyapatite (Hap) or A-type carbonated apatite (ACap) were prepared as described elsewhere (13, 17). Calcium cyanamide was obtained by treatment of calcite by a stream of ammonia between 500 and 850°C (22). The temperature was progressively increased step by step, each step lasted 2 hr.



The so-obtained calcium cyanamide is in fact a mixture of lime and CaCN₂. Carbon and nitrogen analyses of this material reveal that it contains between 50 and 75 wt% of CaCN₂, according to the preparation.

¹A-type carbonated apatite means an apatite, in which carbonate ions substitute for hydroxyl ions along the channels, in opposition to B-type carbonated apatites where carbonate ions replace phosphate ions.

The reaction of ACap with a dry ammonia gas stream was performed in a similar way to the reaction of formation of CaCN₂. The temperature of ACap was gradually increased from 600 to 900°C by step of 50°C: each step lasted approximately 6 hr.

For the reaction of Hap and CaCN₂, a mixture of these components was quickly realized by grinding in an agate mortar: a long grinding was avoided in order to prevent the CaCN₂ hydrolysis by atmospheric moisture (22). The proportions of Hap and CaCN₂ in the mixture were such that there was a large excess of CaCN₂ with respect to Hap, considering the reaction of 1 mole CaCN₂ with 1 mole Hap. The mixture was then pumped off under low pressure (10⁻⁵ Torr) at room temperature, and then heated at 900°C during at least 5 hr under the same pressure. Some experiments were also performed under dry helium, instead of low pressure. The cooling was realized under low pressure or dry helium.

After cooling the resulting products were studied by X-ray diffraction and infrared analyses. Attempts to determine the C and N content on these products were first performed with a CHN apparatus, but a specific method had to be elaborated.

Results and Discussion

1. Treatment of ACap by Ammonia

The effect of ammonia on ACap at high temperature is particularly evidenced by infrared spectrometry (Fig. 1). It clearly appears that this treatment causes a decrease of the intensity of carbonate bands at 880, 1468, and 1532 cm⁻¹ (Fig. 1, spectrum 1), while new bands are increasing at 695, 1960, and 2010 cm⁻¹ (Fig. 1, spectra 2 and 3). The positions of these new bands are in the frequency field of the CN₂²⁻ ion (23).

Infrared observations are corroborated by X-ray investigations: a single phase with an apatitic structure is observed after treatment, and its lattice dimensions are quite

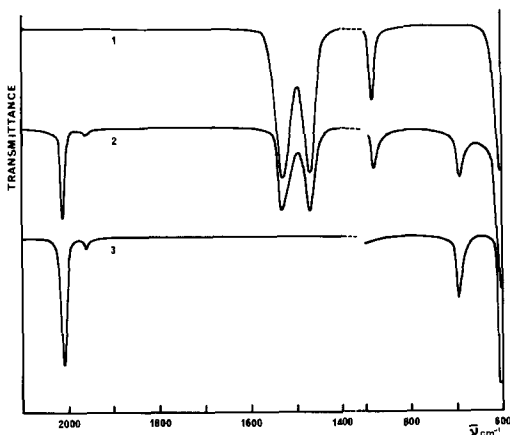


FIG. 1. Infrared spectra: (1) A Cap; (2) and (3) A Cap treated with NH_3 .

different from that of the starting ACap. There are a marked decrease of the a parameter from $a = 9.5_8 \text{ \AA}$ to $a = 9.45_8 \text{ \AA}$ and a slight increase of the c parameter from $c = 6.86_5$ to 6.87_9 \AA . These observations are in agreement with the replacement in the apatite channels, of carbonate ions by smaller ions. So it seems that the treatment of ACap by ammonia leads to a new apatite containing a carbon-nitrogen specie along the channels.

However, some reservations must be noted about this treatment:

(a) The treated products are generally gray-colored, and examination under microscope revealed that this coloration is un-homogeneous. This gray color has been attributed to carbon particles mixed with the apatitic phase. The formation of such carbon particles might be due to a partial decarbonation of the ACap, and to oxydoreduction process of the so-released CO_2 molecules with ammonia at high temperature. It should be noted that this observation has not been realized during the formation of calcium cyanamide. So it is likely that the apatite crystallites play some catalytic effect on the reaction of CO_2 with ammonia: indeed apatites are known to present catalytic properties (24). Our at-

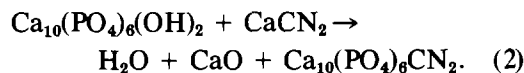
tempts to avoid the formation of carbon particles, were unsuccessful.

(b) The partial decarbonation, which can occur, gives rise to O^{2-} ions, and it is known that these latter ions react very easily with water traces to give hydroxyl ions (17): in fact a low amount of hydroxyl ions was observed by infrared spectrometry on some of the treated samples.

In view of these difficulties in obtaining a pure "carbon-nitrogen" specie containing apatite another method of preparation has been researched.

2. Treatment of Hap by CaCN_2

The product obtained after treatment is colorless. Its X-ray examination indicates the presence of three distinct phases: (a) an apatite, (b) unreacted CaCN_2 , and (c) lime. The presence of unreacted CaCN_2 can be due to the fact that a large excess of this component is used, with respect to Eq. (2), while that of lime can be attributed both to the starting CaCN_2 , which is impure, and to the reaction itself:



In opposition with the carbon particles previously observed, the supplementary phases, CaCN_2 and CaO , can be eliminated easily by treatment of the mixture by ammonium citrate (25), followed by washing with distilled water and drying in an oven at 100°C .

After the latter treatment the product corresponds to a single phase, with an apatitic structure (spatial group $P6_3/m$). The observed interplanar distances and their respective intensities are listed on Table I.

The unit cell dimensions of the so-obtained product are quite different of that of the starting Hap (Table II): an important increase of the a parameter is observed, while the c parameter is only slightly changed. The observations are consistent

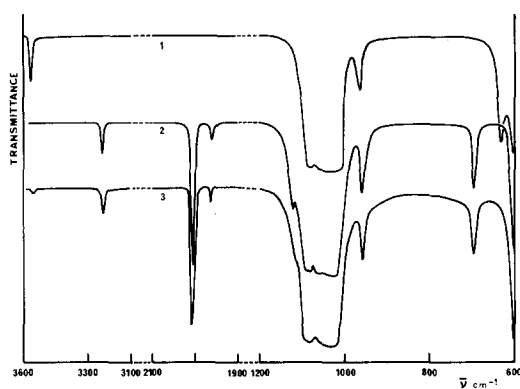


FIG. 2. Infrared spectra: (1) Hap; (2) Hap treated by CaCN_2 under low pressure; (3) Hap treated by CaCN_2 under dry helium.

with the replacement in the apatitic channels of an ion by a bulkier one (26).

These differences between the starting Hap and the treated product are also evidenced by infrared spectrometry (Fig. 2). The hydroxyl bands of Hap at 633 and 3566 cm^{-1} (Fig. 2, spectrum 1) have quite disappeared for the preparation carried under

low pressure (Fig. 2, spectrum 2) while new bands are exhibited at 695, 1120, 1960, 2010, and 3230. Among these new bands, the following ones 695, 1960, 2010, and 3230 cm^{-1} can be attributed to a CN_2^{2-} ion. In fact some of these bands are reported at 620, 2170 cm^{-1} (23), but they lie at 660, 1935, 2040 and 3220 cm^{-1} for the CaCN_2 we prepared. The shift of position between the CaCN_2 lines described in the literature and those we observed is not understood.

However, it remains that the CN_2^{2-} frequencies, of the apatitic phase and those of the calcium cyanamide are different, and this shift may be related to the introduction of the cyanamide ion in the apatite lattice.

An interpretation of the band observed at 1120 cm^{-1} can now be given: in fact some modifications of the infrared spectrum of apatites and more particularly such a band are observed every time the apatites channels are filled with a bivalent ion associated with a vacancy (17, 27). This band is in the field frequency of the PO_4^{3-} vibrations, corresponding to the ν_3 internal mode of the free PO_4^{3-} (28). The fundamental mode ν_3 of the free PO_4^{3-} ion is triply degenerate. The introduction of the PO_4^{3-} ion in the apatitic structure allows a removal of the degeneracy of the formerly degenerate mode of the free ion (29). However, either by considering a site-group or a factor-group analysis, the selection rules for the spatial group $P6_3/m$ allow only three components observable in infra-red for the stretching mode ν_3 (17, 30). With the appearance of a band at 1120 cm^{-1} and its attribution to this mode, four bands are observed in the frequency field 1000–1120 cm^{-1} corresponding to ν_3 .

This apparent contradiction is reflecting the fact that the true unit-cell symmetry must be lower than $P6_3/m$ (17). It is obvious that some symmetry elements ($6_3, \dots$) of the unit-cell are lost, when two hydroxyl groups are substituted by a bivalent ion associated with a vacancy. How-

TABLE I
POWDER DIFFRACTION DATA OF CYANAMIDO
APATITE^a

<i>hkl</i>	<i>d</i>	<i>I/I</i> ₀	<i>hkl</i>	<i>d</i>	<i>I/I</i> ₀
100	8.2 ₀	16	112	2.06 ₃	11
101	5.2 ₇	5	203	2.00 ₁	9
110	4.7 ₄	3	222	1.95 ₀	51
200	4.1 ₀	15	312	1.89 ₇	22
111	3.9 ₀	10	320	1.88 ₁	11
201	3.5 ₂	5	213	1.84 ₃	52
002	3.4 ₄	37	321	1.81 ₅	29
102	3.1 ₇	7	410	1.79 ₀	21
210	3.1 ₀	20	402	1.76 ₁	20
211	2.82 ₆	100	004	1.71 ₀	27
112	2.78 ₂	67	104	1.68 ₃	4
300	2.73 ₄	73	322	1.65 ₁	12
202	2.63 ₅	24			
301	2.54 ₀	7			
212	2.30 ₂	12			
310	2.27 ₅	34			
311	2.16 ₀	14			
302	2.14 ₀	7			

^a $a = 9.47_0 \text{ \AA}$, $c = 6.87_7 \text{ \AA}$; $\text{CoK}\alpha = 1.7889_2 \text{ \AA}$.

ever, if there is a random arrangement of bivalent ions and vacancies along the c axis, the spatial symmetry $P6_3/m$ can be observed statistically for long distances. It is then observable by X-ray diffraction and no surstructure peaks appear.

In fact lowering of the unit-cell symmetry of bivalent ions containing apatites have been observed by X-ray diffraction, in a few cases, and only for stoichiometric compounds: oxypyromorphite (31), strontium phosphate ACap (32) and recently calcium-phosphate ACap (33).

So in some cases infrared appears more sensitive than X-rays to some modifications of the unit-cell symmetry, because infrared observations reflect the single unit-cell symmetry, while X-ray studies show the symmetry over long distances, in comparison with unit-cell dimensions.

In the light of these previous observations, the appearance of a band at 1120 cm^{-1} (Fig. 2, spectrum 2) lends further support to the presence in the apatites channels of bivalent ions associated with vacancies, in order to maintain the charge balance.

The presence of CN_2^{2-} ions along the channels was also checked by the following experiment. Indeed, it is well known that fluorapatite constitutes the most stable apa-

tite, and that if Hap can be converted in chlorapatite and vice versa (34), fluoride ions are not easily displaced from the apatite structure (35). Therefore a mixture of cyanamido-apatite (CN_2ap), and calcium fluoride was realized, and this mixture was treated under low pressure (10^{-5} Torr) at 900°C for 5 hr. After treatment X-ray examination indicates the presence of two phases: (a) a fluorapatite which was characterized by its unit-cell dimensions ($a = 9.37_2\text{ \AA}$; $c = 6.88_8\text{ \AA}$), (b) pure calcium cyanamide.

So it clearly appears that the apatite we prepared by reaction of Hap and CaCN_2 is a cyanamido apatite, in which the CN_2^{2-} ions associated with vacancies are located in the channels.

The problem is then: is this apatite stoichiometric and corresponding to the formula $\text{Ca}_{10}(\text{PO}_4)_6\text{CN}_2\text{O}$? In fact as reported on Table II and Fig. 2 there is some difference between CN_2ap obtained either under low pressure or under dry helium. In the latter case very weak hydroxyl vibrations are still observed (Fig. 2, spectrum 3), while they are not in the former (Fig. 2, spectrum 2). This observation, as well as the difference of unit-cell dimensions of these two products is not sufficient to indi-

TABLE II
TREATMENT OF Hap BY CaCN_2

	Unit-cell dimensions: ($\pm 0.002\text{ \AA}$)		Carbon and nitrogen percentage by weight				
			Method a		Method b		Method c N
	a	c	C	N	C	N	
Starting Hap	9.42 ₁	6.88 ₃					
Samples prepared under low pressure (10^{-5} Torr)	9.46 ₉	6.87 ₇			1.0 ₉	1.2 ₆	2.5 ₆
	9.47 ₆	6.87 ₇	0.1 ₄	0.2 ₆	1.0 ₉	1.3 ₃	2.6 ₁
Samples prepared under dry He	9.45 ₄	6.87 ₉			0.8 ₈	0.9 ₁	2.1 ₀
	9.46 ₈	6.87 ₅	0.1 ₆	0.2 ₇	1.0 ₃	0.8 ₇	2.4 ₄
Theoretical, stoichiometric $\text{CN}_2\text{ ap}$			1.1 ₀	2.7 ₇	1.1 ₀	2.7 ₇	2.7 ₇

cate that the product obtained under low pressure is stoichiometric.

So in order to answer that question we did try to analyse some samples for carbon and nitrogen.

First analyses were performed with a CHN automatic apparatus (Perkin-Elmer-CHN 240) and they gave the results reported in Table II (method a). Indeed both carbon and nitrogen are observed, but their percentages are very low in comparison with the expected results. An interpretation of this discrepancy was found by examination of the solid product after analysis: this product still evidenced CN_2^- , as shown particularly by infrared analysis. But moreover the infrared spectrum of the analyzed product revealed new weak bands at 1250 and 2195 cm^{-1} , the interpretation of which will be given later.

That means that during the analysis with the automatic apparatus, the CN_2ap is not completely decomposed: in fact a run, with such an apparatus lasts a few minutes, and the product is only heated for 2 or 3 min at 1000°C.

So another method was used to study the thermal behavior of the CN_2ap in air. The thermogram is represented in Fig. 3. An increase of weight is first noticed from 700 to 870°C, and then a loss of weight occurs from 870 to 1000°C. After cooling, the final

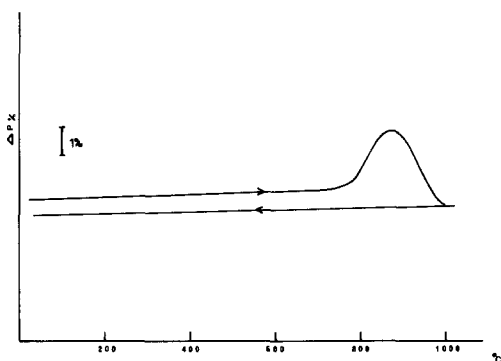
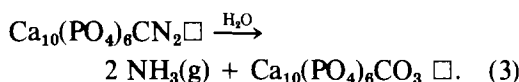


FIG. 3. Thermogravimetric curve of the heating of CN_2ap (air, 300°C/hr).

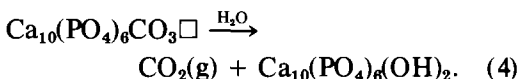
product appears to be Hap, according to its X-ray and infrared examination.

In another experiment, the heating was stopped at the maximum of weight increase: the resulting product is now mainly ACap. On the basis of these observations, an interpretation of the thermal behaviour of CN_2ap can be proposed:

—the first step (weight increase) would be represented by



—the second step (weight loss) would correspond to the hydrolysis of the so-formed ACap:



Taking in account these observations, we did realize a special apparatus for the simultaneous determination of NH_3 and CO_2 . In opposition with the previous automatic apparatus, long runs of heating up to 1100°C are allowed with this apparatus.

The CN_2ap was heated in a flow of nitrogen, free from CO_2 , but charged with water vapor ($p_{\text{H}_2\text{O}} \approx 20$ Torr). The released ammonia was uptaken in hydrochloric acid solution, while the released CO_2 passed through the HCl solution and was adsorbed by soda asbestos in a weighing tube. Results of these analyses are given on Table II (method b).

The observed carbonate percentage is close to the expected one for a stoichiometric product, but the experimental nitrogen percentage is always too low.

An interpretation of the latter difference has been found by considering the following remarks:

(a) the bands previously observed at 1260 and 2195 cm^{-1} for the CN_2ap submitted to a short heating (CHN apparatus) are respectively in the frequency field of nitrite and cyanate ions, in fact such ions NO_2^- and

NCO^- have been previously observed, trapped in the apatitic lattice (36, 37).

(b) the presence of NO_2^- ions in the hydrochloric solution has been ascertained by chemical tests.

These observations indicate that the decomposition of the CN_2^- ion introduced in the apatitic lattice, differs from that of the same ion in CaCN_2 . In the case of apatite, all the nitrogen atoms are not released as NH_3 , according to Eq. (3), but part of the nitrogen is oxidized.

So, in order to get the total amount of nitrogen, of the synthesized $\text{CN}_{2\text{ap}}$, another method of analysis has been used: it consisted in a mineralization method generally used for CaCN_2 (38). This last method gave for the nitrogen the results reported in Table II (method c).

The so-observed values are now in a good agreement with the existence in the lattice of a CN_2^- ion (the C/N atomic ratio is close to $\frac{1}{2}$).

Moreover, on the basis of these results, the $\text{CN}_{2\text{ap}}$ obtained under low pressure appears to be close to the stoichiometry: in fact it contains 0.9_3CN_2^- ion per unit cell.

In order to ascertain this observation, calcium and phosphorus have been analyzed for some samples. The obtained atomic Ca/P ratio is 1.6_9 , which is close from the theoretical value of 1.6_7 . The slight difference may be due either to the analyses accuracy or to a calcium excess. This latter factor is explainable by considering the preparation method: the removal of the calcium excess, by the Silverman's solution, is perhaps not quite complete.

The preparations carried under dry helium are generally less stoichiometric, concerning their CN_2^- content, than those obtained under low pressure, but they still contain, as mentioned above, some hydroxyl ions.

The slight departure from the stoichiometry of the $\text{CN}_{2\text{ap}}$, we obtained, may be responsible to the fact that no lowering of the

symmetry is observable by X-ray diffraction: in fact it is known, that lowering of the apatites symmetry is only observable by this technique for stoichiometric, or very near from the stoichiometry, compounds (32, 33, 39-41).

Conclusions

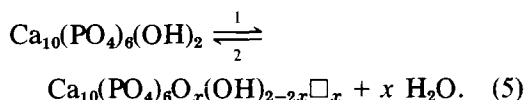
The formation of a cyanamide containing apatite can be realized in two ways:

(a) the treatment of ACap by ammonia at high temperature. The reaction is then difficult and generally incomplete. That may be due to the relative small size of the apatitic channels (2.5 to 3.5 Å) and then to the difficulty of ammonia to diffuse in these channels, without removing carbon dioxide at the same time.

(b) the treatment of Hap by CaCN_2 at high temperature under low pressure.

An interpretation of this last reaction can be given in the following way.

As previously shown (17), low pressure (10^{-5} Torr) heating of Hap results in the following equilibrium:



The dehydration of Hap (way 1) is only complete at 800-900°C under low pressure but the so formed oxyapatite ($x = 1$, Eq. (5)) will undergo a partial rehydration during cooling, even under low pressure.

The extreme reactivity of oxyapatite or of oxyhydroxyapatites is particularly evidenced by this last rehydration, but it is also revealed by the formation of other apatites such as ACap or peroxi-apatite (17).

In a dry CO_2 or O_2 flow at 800-1000°C, the dehydration of Hap will occur Eq. (5). But in this case, the CO_2 or O_2 molecules will diffuse along the channels, and be uptaken by the formed O^{2-} ions to give respectively rise to CO_3^{2-} or O_2^{2-} ions, which stabilize the lattice.

In a similar way, we have previously shown that the treatment at 1000°C under low pressure, of a mixture of Hap and CaS resulted in the formation of a sulfide apatite mixed with lime (17). The involved reaction is then a solid-state exchange between the O²⁻ ions of oxyapatite or oxyhydroxyapatite, and the S²⁻ ions of CaS.

The formation of CN₂ap appears to be similar to that of sulfide apatite: an ion exchange must take place between the O²⁻ ions of apatite and the CN₂²⁻ ions of calcium cyanamide.

This possibility of exchange at high temperature between two solid phases may be related to the following observations:

—the presence in the apatite structure of channel-like ways running all along the crystallites' length, and constituting easy pathways for diffusion phenomena;

—the high reactivity or instability of Oxap, which may be due to the small size of O²⁻ ions (1.40 Å) (42) and to the fact that each O²⁻ ion is associated to a vacancy.

The substitution of O²⁻ ions by bulkier ones, S²⁻ and CN₂²⁻, will probably maintain the structure better than do O²⁻ ions.

The decomposition of CN₂ap appears to be different from that of CaCN₂. First CN₂ap is not hydrolyzed at room temperature as CaCN₂ is, its hydrolysis begin only at 700°C in air. Secondly during the hydrolysis of CN₂ap, NH₃ is not the only nitrogen species formed, but a dismutation of nitrogen must take place, giving rise to ammonia and nitrogen oxide.

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