



HOKKAIDO UNIVERSITY

Title	RAPID HYDROGEN RANDOMIZATION IN AMMONIA
Author(s)	MIYAHARA, Koshiro; OZAKI, Atsumu; KIMURA, Takeo
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 11(2), 124-129
Issue Date	1963-11
Doc URL	https://hdl.handle.net/2115/28058
Type	departmental bulletin paper
File Information	11(2)_P124-129.pdf



Short Note

RAPID HYDROGEN RANDOMIZATION IN AMMONIA

By Koshiro MIYAHARA^{*)}, Atsumu OZAKI^{**)}
and Takeo KIMURA^{***)}

(Received June 19, 1968)

A remarkable memory effect observed in the case of mass spectrometric measurements of ammonia has given rise to a question how far the equilibrium composition of mixture $\text{NH}_3^{(H,D)}$ of NP_3 , NP_2D , NPD_2 and ND_3 by a mere process of putting ND_3 to mass spectrometric measurement.

It has now been confirmed that the composition of NH_3 corresponds to the equilibrium distribution whether the sample of ammonia be ND_3 directly put to mass spectrometric measurement or resultant ammonia of exchange reaction between NP_3 and D_2 conducted in the presence of metallic catalysts. Fig. 1 shows the mole percents of NP_3 , NP_2D , NPD_2 and ND_3 in NH_3 observed by mass spectrometer versus its overall deuterium percent; a), b) and c) show the results obtained from resultant NH_3 of exchange reaction conducted in the presence of metallic catalysts indicated in the Figure, while d) and e) refer to the results of mere process of putting ND_3 to mass spectrometric measurement. Full lines show the equilibrium values calculated by assuming the random distribution of deuterium over NH_3 -molecules. Mass spectrometers used in the above five cases are different from each other and the electron accelerating voltage has been kept for every case so low as to suppress fragmentation and recombination of ammonia in the ionization chamber and to obtain a spectrum consisting of peaks of parent ion NH_3^+ alone. In the case of d) furthermore the mass spectrometer was improved to reduce its catalytic activity by the use of a gold orifice and coating the inner surface of the ionization chamber with gold. The results of Fig. 1 show that mass spectrometric measurement of deuterioammonia results inevitably in the random distribution of deuterium accompanied with a remarkable depression of deuterium content.

REDING and HONIG⁴⁾ have found by infrared absorption spectrometry that an equimolar gaseous mixture of NP_3 and ND_3 was converted in a glass vessel into an equilibrium mixture of NP_3 , NP_2D , NPD_2 and ND_3 at room temperature within a week after mixing. One of the present authors (K.M.) reexamined their results⁴⁾

*) Research Institute for Catalysis, Hokkaido University, Sapporo.

**) Tokyo Institute of Technology, Tokyo.

***) H represents protium P and deuterium D.

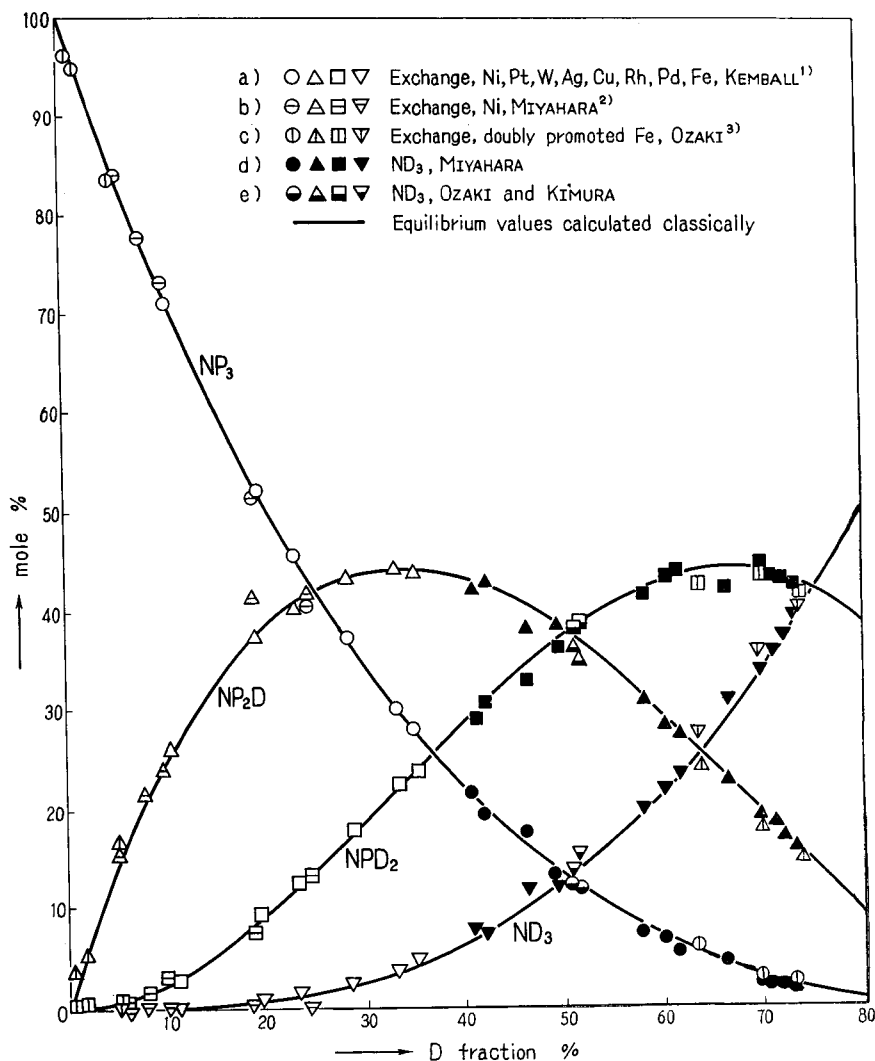


Fig. 1. The results of mass spectrometric measurements of ND₃ in comparison with those of the resultant ammonia of catalyzed exchange reaction between NP₃ and D₂ in the presence of metallic catalysts.

and found that the above hydrogen randomization was completed in a glass vessel, preliminarily evacuated at 300°C to 1×10^{-6} mmHg, instantaneously on mixing at room temperature as shown in Figures 2, 3, 4 and 5. Fig. 2 or 3 shows the degenerated deformation band of the infrared absorption spectrum of NP₃ (1630 cm^{-1}) or ND₃ (1190 cm^{-1}) respectively. ND₃ sample used for this observation was newly

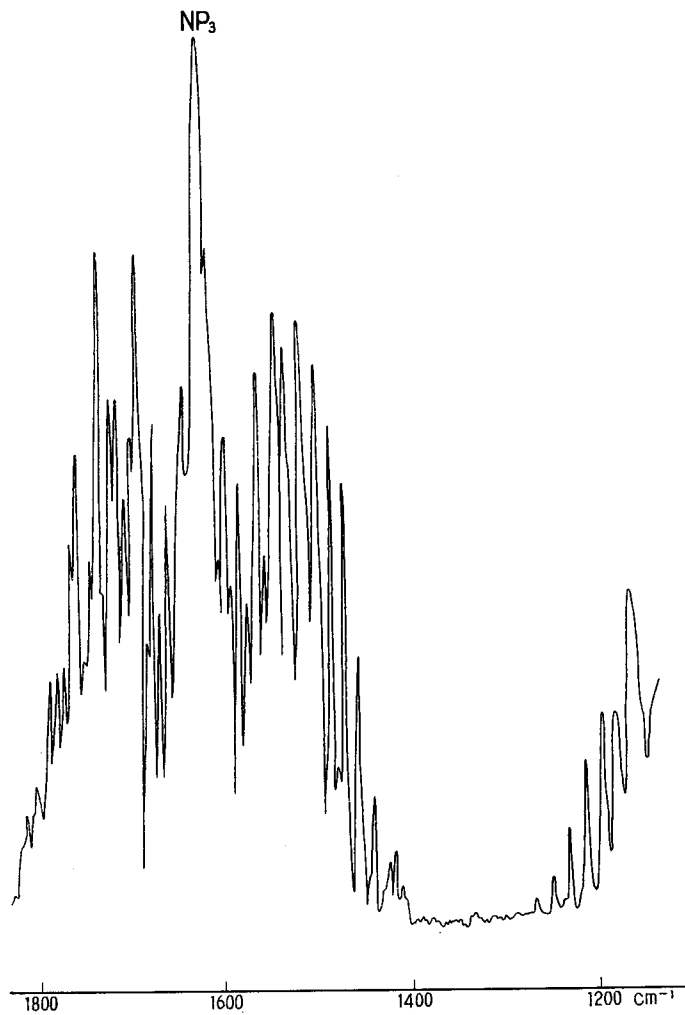


Fig. 2. Infrared absorption spectrum of NP_3 .

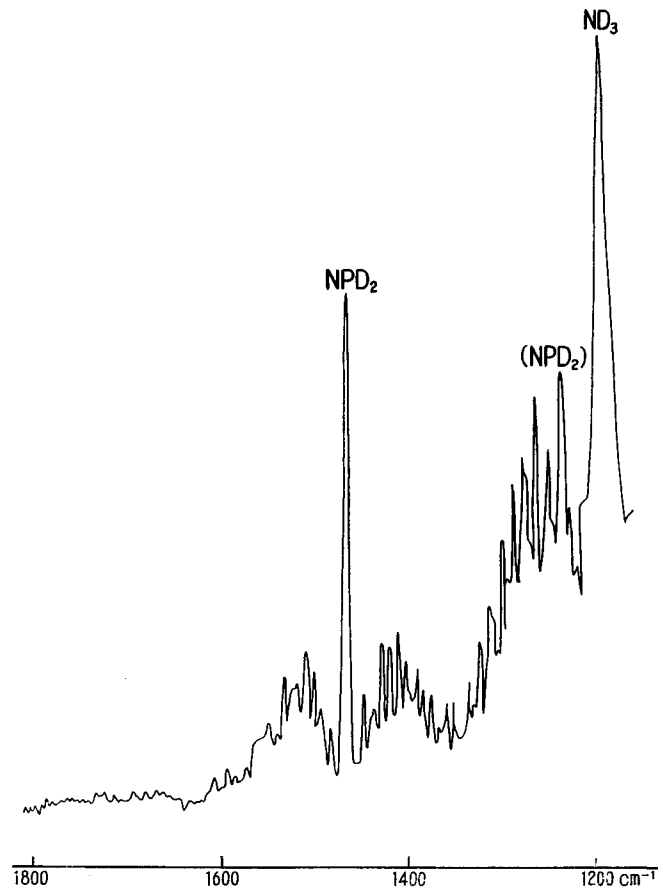


Fig. 3. Infrared absorption spectrum of ND_3 .

Short Note

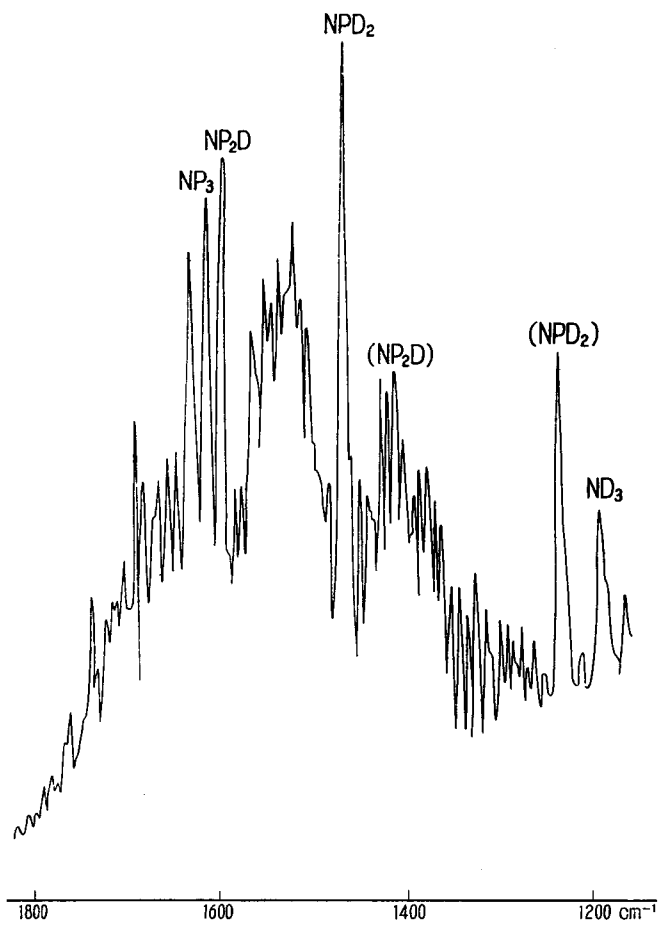


Fig. 4. Infrared absorption spectrum of a mixture of NP_3 and ND_3 just after mixing.

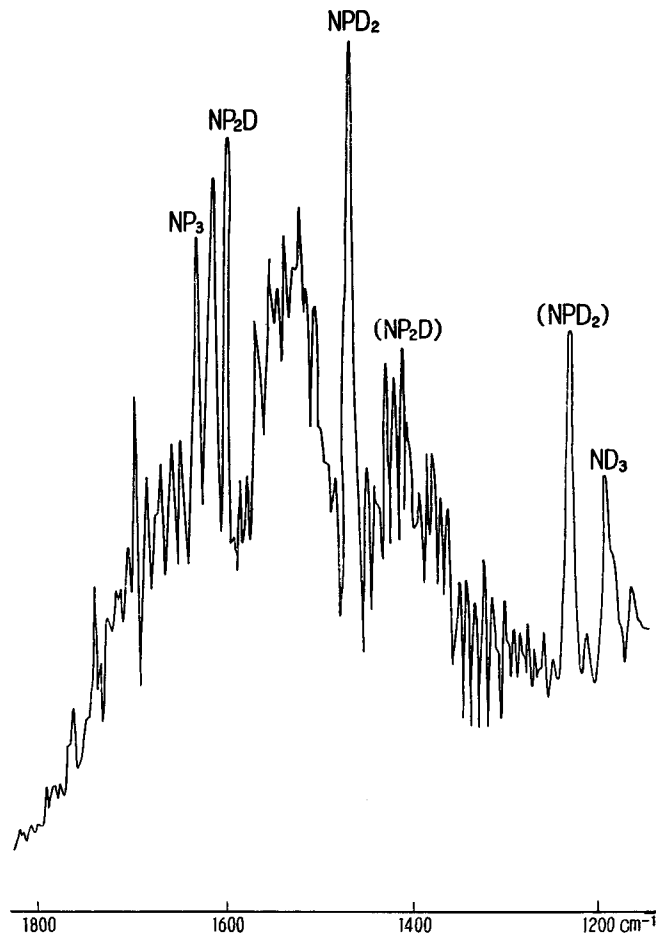


Fig. 5. Infrared absorption spectrum of the same sample as that of Fig. 4 after being heated at 200°C in a glass vessel for 5 minutes.

Short Note

made from heavy water and magnesium nitride and contained considerable amount of NPD_2 (1470 cm^{-1}) as shown in Fig. 2. Fig. 4 is a spectrum of a mixture of NP_3 and ND_3 obtained just after mixing and Fig. 5 is that obtained after heating the same sample at 200°C for five minutes in the same glass vessel as used for mixing. Fig. 4 and 5 are identical with each other with weak bands for NP_3 and ND_3 and strong ones for NP_2D (1600 cm^{-1}) and NPD_2 , showing that the mixture gas completed the hydrogen randomization in ammonia instantaneously on mixing at room temperature.

One of the present authors (K. M.) has found that hydrogen exchange between D_2 and NP_3 did not practically take place in a mass spectrometer or in a glass vessel even at 150°C . This result shows that chemisorbed hydrogen, if any, is not responsible for the observed rapid hydrogen randomization in ammonia or such dilution of deuterium in ND_3 by protium in a mass spectrometer. The latter result might hence be due to water held by metal or glass.

KEMBALL¹⁾ has examined the catalytic hydrogen exchange between D_2 and NP_3 on various evaporated metal films and found that the relative abundances of respective deuterioammonias formed with different metals under different conditions could be plotted on same curves by a suitable selection of the time scale, as shown in Fig. 1. He concluded from this result a mechanism that a single hydrogen atom was exchanged between hydrogen and ammonia molecules by one act of the reaction. Plots b) in Fig. 1 is the results obtained by one of the present authors (K. M.)²⁾ of the same hydrogen exchange catalyzed by evaporated nickel film, and plots c) in the same figure the results of the present author (A. O.)³⁾ for the same reaction catalyzed by doubly promoted ammonia synthetic catalyst. All of these plots are coincident with theoretical curves of the random distribution of hydrogen in ammonia similarly as those of mass spectrometric measurements of ND_3 mentioned above, which shows that these observed distributions of deuterioammonias are due to the rapid hydrogen randomization in ammonia in a mass spectrometer. Consequently any reaction mechanism could not be deduced from above results of distribution of deuterioammonias thus observed^{1,2)}. Previous analysis of experimental results by one of the present authors (K. M.)²⁾ will be corrected in the next short note with due regard to the above effect.

The authors wish to express their sincere thanks to Professor Juro HORIUTI for his helpful discussion, to Dr. S. MATSUSHITA and Miss. T. NAKATA both in Department of Chemistry, Faculty of Science, Hokkaido University for their kind helps of measuring infrared absorption and especially to Toyo Rayon Foundation for the Promotion of Science and Technology for a grant by which a mass spectrometer of type Hitachi RMU-6 was purchased.

References

- 1) C. KEMBALL, *Trans. Faraday Soc.* **48**, 254 (1952); *Proc. Roy. Soc. A* **214**, 413 (1952).
- 2) K. MIYAHARA, *This Journal* **9**, 159 (1961).
- 3) A. OZAKI and T. KIMURA, unpublished.
- 4) F. P. REDING and D. F. HONIG, *J. Chem. Phys.* **23**, 1053 (1955).

ON THE HYDROGEN EXCHANGE BETWEEN DEUTERIUM AND AMMONIA CATALYZED BY EVAPORATED NICKEL FILM

By Koshiro MIYAHARA

(Received June 19, 1963)

In the previous short note¹⁾ it was shown that rapid hydrogen randomization in ammonia takes place in a mass spectrometer used for measurement, which invalidated any reaction mechanism^{2,3)} of catalyzed hydrogen exchange between deuterium and ammonia deduced from the distribution of deuterioammonias thus observed.

It was found, on the other hand, that the relative abundances of P₂, PD and D₂, where P or D denotes protium or deuterium respectively, were practically not affected by a mass spectrometer, providing hence a sound basis of analyzing the mechanism of the exchange. Table 1 reproduces the initial rate $V_0^{P_2}$, V_0^{PD} or $V_0^{D_2}$ of evolution of P₂, PD or D₂ respectively observed in the previous experiments with an evaporated nickel film³⁾, which were corrected for change of catalytic activity by multiplying observed values of $V_0^{P_2}$ etc. in the second or the third series by the ratio of the rate of a standard reaction conducted prior to the first series to the rate of the same standard reaction conducted prior to the latter series. The rate of the standard reaction was given by the amount of [PD]/[D₂] in 3:1 mixture of D₂ and NP₃ at 44 mmHg total pressure observed at 100°C, 5 minutes after the latter mixture being brought into contact with the catalyst, where [PD] or [D₂] is the concentration of PD or D₂. The y^D in Table 1 is the fraction of the number of adsorbed deuterium D(a) over the sum of the numbers of D(a) and adsorbed protium P(a), which was calculated by the relation derived in the previous paper ignoring isotopic difference³⁾ that

$$y^D = V_0^{PD}/(2V_0^{P_2} + V_0^{PD}). \quad (1)$$

V_0^P in Table 1 is the initial increasing rate $100(2V_0^{P_2} + V_0^{PD})/2[H_2]$ of P atom percent in hydrogen gas, where H represents P and D.