

An ESR Study of Radicals Produced in γ -Irradiated Ammonia-Boron Trifluoride, NH_3BF_3 , and ND_3BF_3

Kunihisa SOGABE*

Abstract: ESR spectra of radicals produced in ammonia-boron trifluoride, NH_3BF_3 , and ND_3BF_3 subjected to γ -irradiated at 77 K were observed. From analyses of these spectra, the radicals were identified as a BF_3^- or a NH_3BF_3^- and a $\cdot\text{NHBF}_2$. The latter radical is interpreted to be prepared by a loss of a hydrogen from NH_2BF_2 , which was produced by the decomposition of the NH_3BF_3 . ESR parameters of the $\cdot\text{NHBF}_2$ radical were $a_F=26$ G, $a_B=36$ G, $a_N=260$ G, and $a_H=41$ G, respectively. These results show that a dative bond of the NH_3BF_3 differs from that of the NH_3BH_3 in the bond strength, although both bonds are stronger than a P-B dative bond in phosphine-boranes under γ -irradiation.

Introduction

Boron halides or boranes in which boron atom is short of two electrons having complete valence shell could produce many interesting addition products (adducts) with all molecules containing an unshared electron pair. In particular, ammonia-boron trifluoride (NH_3BF_3) or ammonia-borane (NH_3BH_3) were recognized to possess a nitrogen-boron dative bond and a staggered configuration with C_{3v} symmetry by intensive studies on X-ray diffractions,^{1,2)} NMR,³⁾ IR spectra,⁴⁾ or theoretical calculations.^{5,6)}

Armstrong and Perkins⁵⁾ recently reported that boron trifluoride would be transformed a planar configuration (D_{3h}) into a pyramidal form (C_{3v}) on the NH_3BF_3 adduct formation and at this time, 0.23 electron would be transferred from NH_3 to BF_3 . These adducts, therefore, seems to involve similar a weak dative bond with phosphine-borane adducts in which a phosphorus-boron bond with incomplete sharing of electron pair were easily broken to produce phosphoranyl radicals under γ -irradiation.⁷⁾

However, Hasegawa⁸⁾ more recently reported

that a radical produced by γ -irradiation of diborane, B_2H_6 , at 77 K was not BH_3 radical formed by a symmetrical cleavage of a B-B bond but a $\cdot\text{B}_2\text{H}_5$ by an extraction of one of two bridged hydrogens. Lovas and Johnson,⁹⁾ also, established that N-B bond in amino-fluoro borane, NH_2BF_2 , produced during the gas phase reaction of NH_3 and BF_3 is fairly strong. These observations may suggest an existence of an alternative nature to that proposed by Armstrong and Perkins⁵⁾ on the N-B dative bond in the NH_3BF_3 adduct. Ammonia-borane is known to be isoelectric and to possess the same configuration with C_2H_6 molecule, which is irradiated by γ -rays to produce an ethyl radical. Nevertheless, the isoelectronic amine borane radicals are received little attention. The unpaired electron serves a measure of variations for the electron distribution in an interesting radical and ESR parameters reflect the actual electronic environments within this adduct. The NH_3BF_3 , together with the NH_3BH_3 , is therefore investigated in this paper for identifications of radicals and an evaluation of a nature on the N-B dative bond.

Experimental

Ammonia-boron trifluoride adduct was

* Laboratory of Chemistry, Faculty of Education, University of Shimane, Matue, 690 Japan.

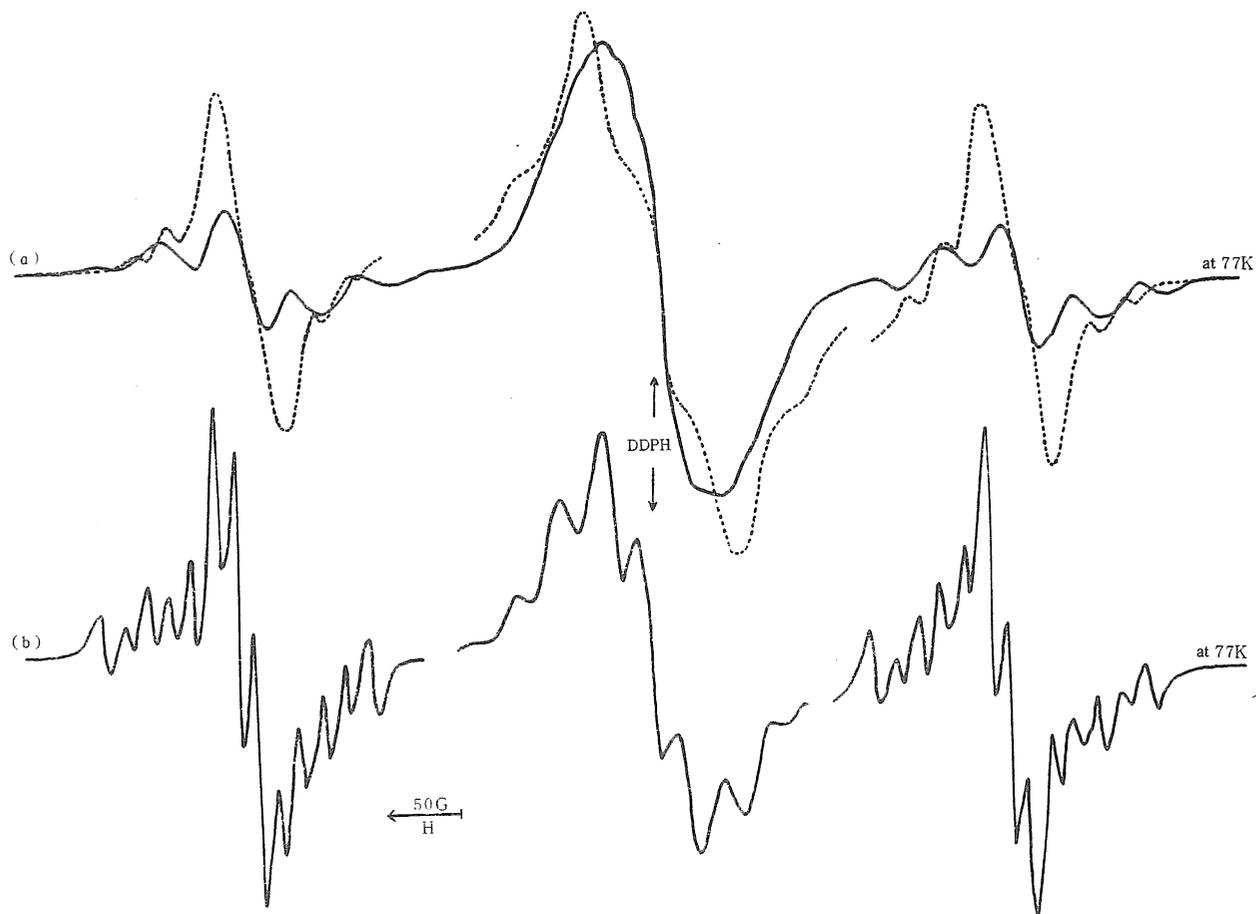


Fig. 1 ESR spectra of γ -irradiated (a) polycrystalline of NH_3BF_3 (full line) and ND_3BF_3 (dotted line) (b) single crystal of NH_3BF_3 .

prepared by the reaction between ammonia and boron trifluoride etherate $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ at -78°C . ND_3BF_3 was prepared in a similar way by the use of deuterio ammonia, ND_3 . Deuterio ammonia gas was made synthetically by the reaction of a freshly prepared magnesium nitride with heavy water. NH_3BH_3 was prepared from NH_4Cl and LiBH_4 and was separated from LiCl by filtration at -78°C .¹⁰⁾ All obtained adducts were washed with anhydrous ether and dried *in vacuo* for *ca.* 24hr. Single crystal of NH_3BF_3 was prepared from anhydrous acetone. BF_3 gas (99.7%) was obtained commercially and purified before use by a trap-to-trap fractionation. D_2O (99.5%) and LiBH_4 obtained from Merck Sharp & Dohme of Canada. Ether and acetone were distilled and stored over sodium metal. A conventional high-vacuum line employing greaseless stopcocks was used to prevent decomposition of boron compounds.

Sample was introduced in an ESR tube and sealed off *in vacuo*. Then sample was irradiated with ^{60}Co γ -rays at 77 K for *ca.* 40hr at dose rate of 10^6 rad/h. ESR spectra were measured at 77 K with no warm up and at various temperature with standard variable temperature attachments. The purity of the sample was checked by means of powder X-ray diffraction and mass spectrometer.¹¹⁾ For comparison, X-ray diffraction powder pattern and ESR spectrum on ammonium borofluoride, NH_4BF_4 were observed.

Results and Discussion

An ESR spectrum of the γ -irradiated $\text{NH}_3\text{-BF}_3$ in polycrystalline observed at 77 K with no warm up is shown in Fig. 1. The spectrum generally consisted of three components, in which relative weak two outer components with symmetric quintet features have a separation of *ca.* 520 G and a relative intense inner one has a total linewidth of *ca.* 200 G. By raising temperature of the sample, the inner component was present to *ca.* 400 K without a change of features, while the outer

ones were annealed completely at *ca.* 170 K. A residual signal was in accord with that observed when the sample was irradiated at room temperature. This signal is interpreted to result from a BF_3^- or NH_3BF_3^- radical since these radicals may be produced by a decomposition of this adduct under γ -irradiation but discussion is put away in this paper.

An unstable radical species is of interest and a detailed discussion will be developed here. The central position of the outer two signals is placed at lower field than DDPH by *ca.* 20 G. This may be caused by effects of a second-order perturbation which are often observed in the cases of a nucleus with a nuclear spin more than $I=1$. In this case, a B nucleus ($I=3/2$), a N nucleus ($I=1$), two equivalent F nuclei ($2I=1$), or two equivalent H nuclei ($2I=1$) are involved but the B nucleus is excluded because of being unable to find up a quartet with a total separation of *ca.* 520 G in this spectrum. This spectrum is, therefore, consisted of a triplet in which a central component ($M_I=0$) disappeared behind π -radical with a relative intensity.

An ESR spectrum of a γ -irradiated ND_3BF_3 shown in Fig. 1 (b) was observed to determine the nuclear showing the effects of the second-order perturbation. In addition to the central intense signal due to the π -radical, the two components being subdivided to a quintet were observed with a slight change in line width, while the coupling of the triplet remained unchanged. It became clear to exclude the splitting due to a hydrogen nuclear from the coupling of the triplet but to include in that of the quintet. An exchange of a hydrogen to a deuterium resulted in only change in line width, for which the author deduced that a coupling for a hydrogen must be *ca.* 40 G. Accordingly, the triplet are considered to be formed by either a nitrogen or two equivalent fluorine nuclei.

To further identify this radical species, an ESR spectrum of a γ -irradiated single crystal

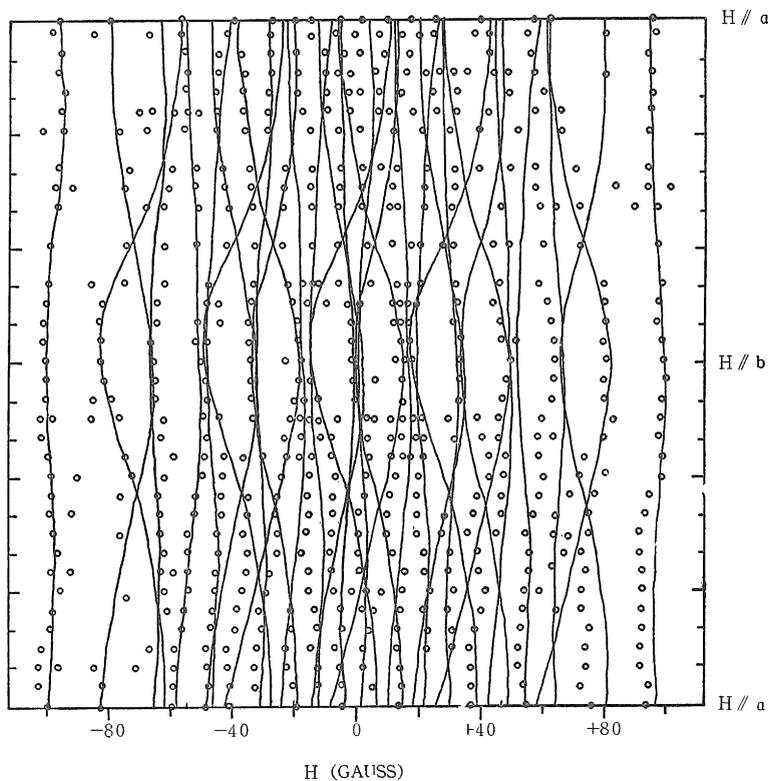


Fig. 2 Angular dependences about b axis of γ -irradiated single crystal of NH_3BF_3 . The parts only in the lower field side are shown.

of NH_3BF_3 was similarly observed. This spectrum obtained at the direction of being parallel to b axis of single crystal is shown in Fig. 1 (c). Angular dependences about b axis were measured and low field component only in the triplet is shown in Fig. 2. Analyses of other two orthogonal axes were unsuccessful. In Fig. 2, however, three kinds of doublet were found. Two doublets are composed of two nuclei having a nuclear spin of $I=1/2$, with a relative anisotropy, while one doublet is attributed to a nuclear having a nuclear spin of $I=1/2$, with no anisotropy and the coupling of $ca.$ 40 G. The coupling of the hydrogen nuclear is $ca.$ 40 G and then the doublet with no anisotropy is identified to arise from the hydrogen nuclear. Two doublets with anisotropy are therefore determined to result from two fluorine nuclei.

Furthermore, figure shows to involve of a quartet of three kinds of doublet and this quartet is assumed to arise from a B nucleus with a nuclear spin of $I=3/2$. A residual nuclear is a nitrogen with a nuclear spin of $I=1$ and the triplet having separation $ca.$ 260 G is therefore considered to arise from the N nuclear.

From the analyses of the spectrum, the radical obtained here is interpreted to be $\cdot\text{NHBF}_2$ produced by a loss of a hydrogen atom from NH_2BF_2 which might be formed by an elimination of HF from NH_3BF_3 under γ -irradiation.

The s character of the nitrogen nuclear in the $\cdot\text{NHBF}_2$ radical is therefore calculated to be 47%. This result is particularly surprising in view of the fact that this radical contains a sp hybrid on nitrogen. To judge the

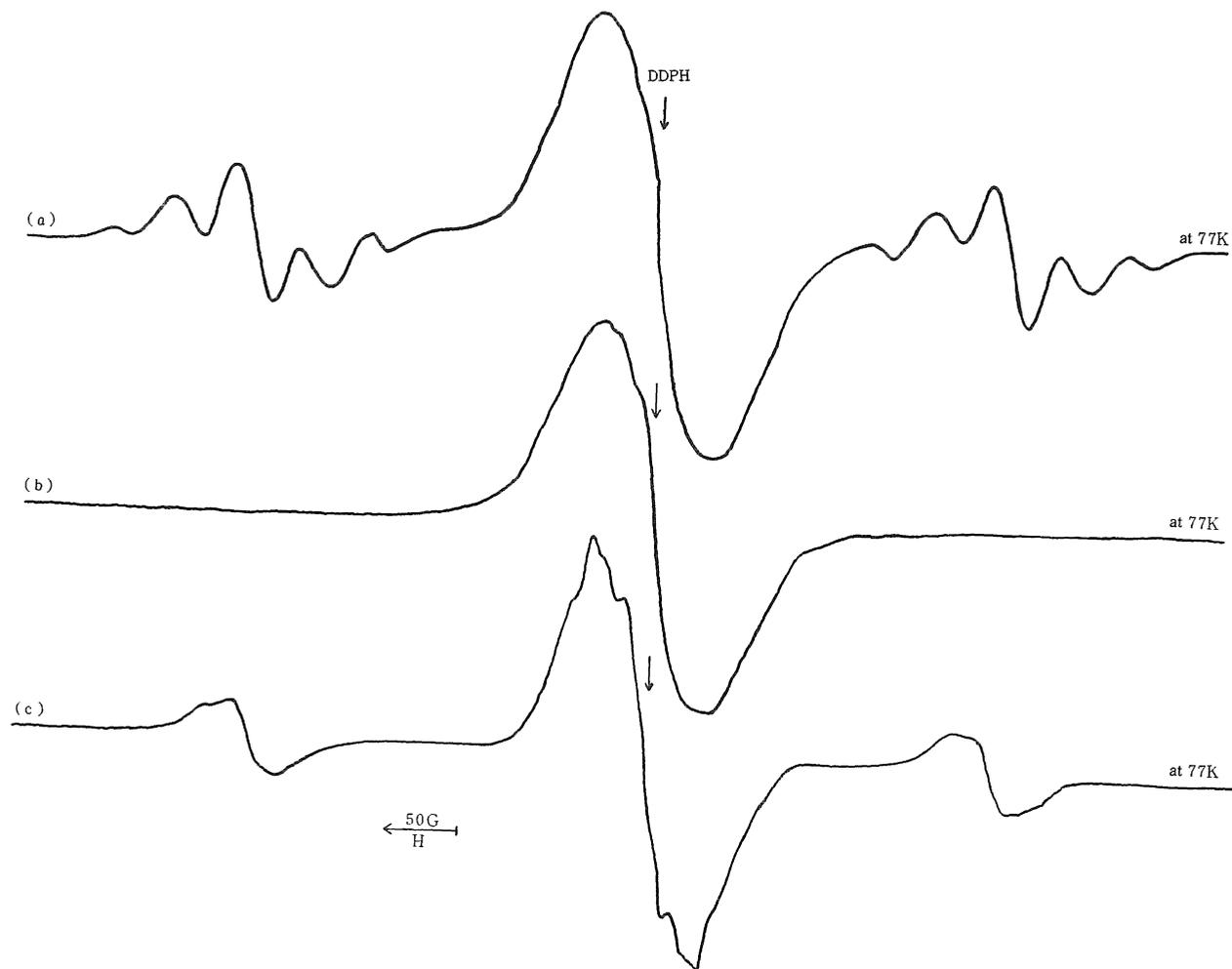
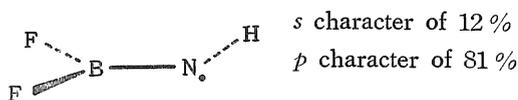


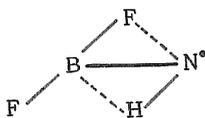
Fig. 3 ESR spectra of γ -irradiated polycrystalline of (a) NH_3BF_3 , (b) NH_3BH_3 , and (c) NH_4BF_4

correctness of such an assignment of this radical species, ESR spectra of γ -irradiated NH_3BH_3 and NH_4BF_4 in polycrystalline shown in Fig. 3 were observed. Signal attributed to the $\cdot\text{NHBF}_2$ radical were also observed in the case of NH_4BF_4 , but no signal attributed to a $\cdot\text{NHBH}_2$ one was observed in NH_3BH_3 . From these results, a NH_3BH_3^- or other π -radical is interpreted to be mainly produced by γ -irradiation of the NH_3BH_3 and to exhibit the signal shown in Fig. 3 (b). The NH_3BH_3^- radical was postulated by Claxton *et. al.*,¹²⁾ who more recently reported the formation of the $\cdot\text{NMe}_2\text{BH}_3$ radical from stable adduct, NMe_3BH_3 . The NH_3BF_3 adduct first decomposes to NH_2BF_2 and then the $\cdot\text{NHBF}_2$ radical is produced by the extraction of the hydrogen atom from the NH_2BF_2 under γ -irradiation, while no decomposition of the NH_3BH_3 adduct proceeds to a NH_2BH_2 .

The aminodifluoro borane was known to possess a planar structure⁹⁾ and in order to approach the experimental data, INDO-UHF calculations on various planar configurations of the $\cdot\text{NHBF}_2$ radical were carried out by using structure parameters reported by Lovas and Johnson.⁹⁾ The s character of the N nuclear calculated by INDO-UHF method are 12% at the most in spite of many attempts and are made no comparison with those estimated from the ESR spectrum.



This radical is assumed to possess a structure described below and so on, although calculations are still not performed.



This radical is of very interesting for the radical having the sp hybrid on the nitrogen but is still not completely elucidated. Accordingly, many experiments on single crystal of ND_3BF_3 and NH_3BH_3 , together with NH_3BF_3 , and INDO calculations on another possible form of the $\cdot\text{NHBF}_2$ radical will be performed to perfectly identify this radical.

ACKNOWLEDGMENT : Present author is deeply grateful to Dr. A. Hasegawa and K. Takeda of Hiroshima University, and Professor M. Miura of Okayama Science College for their valuable discussions and continued cooperation.

References

- 1) J. L. Hoard, S. Geller, and W. M. Cashin : *Acta. Cryst.*, **4**, 396 (1951).
- 2) W. J. Jenkins : *J. Amer. Chem. Soc.*, **78**, 5500 (1956) R. W. Parry, G. Kodama, and D. R. Schultz : *J. Amer. Chem. Soc.*, **80**, 24 (1958) ; A. P. Caron, J. L. Ragle, M. E. Yorke, and H. Yen : *J. Phys. Chem.*, **72**, 556 (1968).
- 3) C. W. Heitsch : *Inorg. Chem.*, **4**, 1019 (1965). J. B. Leane and R. E. Richards : *Spectrochimica Acta.*, **10**, 154 (1957).
- 4) J. Goubeau and H. Mitschelien : *Z. Physik Chem.*, **14**, 61 (1958).
- 5) D. R. Armstrong and P. G. Perkins : *Inorg. Chim. Acta.*, **10**, 77 (1974).
- 6) A. A. Frost : *Theoret. Chim. Acta*, **18**, 156 (1970).
- 7) K. Sogabe : *J. Sci. Hiroshima Univ., Ser. A*, **39**, 11 (1975).
- 8) A. Hasegawa and J. Sohma : *Mol. Phys.*, **20**, 118 (1972).
- 9) F. J. Lovas and D. R. Johnson : *J. Chem. Phys.*, **59**, 2347 (1973).
- 10) S. G. Shore and R. W. Parry : *J. Amer. Chem. Soc.*, **80**, 8 (1958).
- 11) P. A. Barfield, M. F. Lappert, and J. Lee : *J. Chem. Soc., A*, 554, (1968) E. F. Rothgery, H. A. Mcgee, Jr., and S. Pusatcioglu : *Inorg. Chem.*, **14**, 2236 (1975).
- 12) T. A. Claxton, S. A. Claxton, S. A. Fieldhouse, R. E. Overill, and M. C. R. Symons : *Mol. Phys.*, **29**, 1453 (1975).