June, 1972] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1595—1598(1972) 1595

The Infrared Spectra of Addition Compounds of Hydrogen and Deuterium Cyanides with Boron Tribromide

Isao KANESAKA, Yoshiyuki HASE, and Kiyoyasu KAWAI
Faculty of Literature and Science, Toyama University, Gofuku, Toyama

(Received August 10, 1971)

The infrared spectra of addition compounds of hydrogen and deuterium cyanides with boron tribromide have been measured in the frequency region from 4000 to 200 cm^{-1}, and the normal frequencies have been proposed on the basis of the C_{3v} symmetry for four isotopic compounds, $HCN\cdot{}^{10}BBr_3$, $HCN\cdot{}^{11}BBr_3$, $DCN\cdot{}^{10}BBr_3$, and $DCN\cdot{}^{11}BBr_3$. The force constants have been calculated on the assumption of a modified Urey-Bradley force field, and the shift of the vibrational frequencies by the coordination has been discussed.

The infrared spectra of the addition compounds of hydrogen and deuterium cyanides with boron trichloride have been studied previously, and the observed spectra have been assigned on the basis of the C_{3v} symmetry, the isotopic effect of H and D or of ^{10}B and ^{11}B being taken account of.[1] The force constants of those compounds have also been calculated.[2]

In many of the addition compounds of $R-C\equiv N$ with metal halides, in which R is H, D, Cl, Br, CH_3, or C_6H_5, the $C\equiv N$ stretching frequency has been found to become higher than that of the parent $R-C\equiv N$.[1,3-9] Purcell and Drago[8] have explained that the shift of the $C\equiv N$ stretching frequency in the addition compounds of acetonitrile is due mainly to the increase in the $C\equiv N$ stretching force constant by coordination. In the addition compounds of hydrogen and deuterium cyanides, however, it has been found that the shift is due mainly to the mechanical coupling and only partly to the increase in the force constant.[1,2] The vibrational spectra of the addition compounds of trimethylamine with boron trihalides have been studied in detail, and the vibrational assignments of the observed frequencies have been proposed on the basis of the isotopic shift and the trend of the frequencies.[10]

In the present paper, the infrared spectra of the addition compounds of hydrogen and deuterium cyanides with boron tribromide will be studied, and the force constants of those compounds will be calculated.

Experimental

The hydrogen cyanide, deuterium cyanide, and boron tribromide were prepared by the ordinary method and were purified by fractional distillation *in vacuo*. The addition compound, $HCN\cdot BBr_3$ or $DCN\cdot BBr_3$, was prepared by the reaction of boron tribromide dissolved in cyclopentane with hydrogen or deuterium cyanide, after the method described by Woolf[11] in his study of the addition compounds of cyanogen halides.

The addition compounds were covered with cyclohexane or carbon tetrachloride to prevent them from hydrolysis and were then dispersed on KRS-5 plates, and their infrared

TABLE 1. THE ASSIGNMENT OF THE INFRARED SPECTRA OF $HCN\cdot BBr_3$ AND $DCN\cdot BBr_3$ (cm^{-1})

Obsd		Assignment$^{a)}$
$HCN\cdot BBr_3$	$DCN\cdot BBr_3$	
3120 s	3120* w	$\nu(C-H)$
	2594 s	$\nu(C-D)$
2197 s	2200* w	$\nu(C\equiv N)$
	1942 s	$\nu(C\equiv N)$
1110 w		750+363=1113
	1089 w	776+317=1093
795 w		$\delta(HCN)$
777 w	776 w	$\nu(N-{}^{10}B)$
750 s	749 s	$\nu(N-{}^{11}B)$
696 s	696 s	$\nu({}^{10}B-Br)$ asym.
674 vs	674 vs	$\nu({}^{11}B-Br)$ asym.
	656 m	$\delta(DCN)$
662 vw		$363+2\times150=663$
632 vw		$2\times318=636$
560 vw		$3\times188=564$
501 vw		318+188=506
	496 vw	350+150=500
	396 vw	$2\times198=396$
375 vw		$2\times188=376$
	372 vw	198+174=372
363 m	350 w	$\delta(CNB)$
333 vw		188+150=338
318 s	317 s	$\nu(B-Br)$ sym.
300 vw	300 vw	$2\times150=300$
207 vw	198$^{c)}$	$\delta(NBBr)$sym.
188$^{c)}$	174$^{c)}$	$\delta(NBBr)$ asym.
150$^{c)}$	150$^{c)}$	$\delta(BrBBr)$ asym.

a: When the frequencies are same for the compounds of boron ten and boron eleven, boron atom is simply indicated as B.
c: Assigned from combination bands. *: Assigned to the impurity.
vs=very strong, s=strong, m=medium, w=weak, and vw=very weak.

---

1) K. Kawai and I. Kanesaka, *Spectrochim. Acta*, **25A**, 1265 (1969).

2) Y. Hase and I. Kanesaka, *Nippon Kagaku Kaishi*, to be published.

3) H. J. Coerver and C. Curran, *J. Amer. Chem. Soc.*, **80**, 3522 (1958).

4) W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, **1960**, 2182.

5) D. S. Bystrov and B. K. Nazarov, *Dokl. Akad. Nauk SSSR*, **148**, 1335 (1963).

6) E. Allenstein and A. Schmidt, *Chem. Ber.*, **97**, 1863 (1964).

7) E. Oikawa and S. Kambara, *J. Polymer Sci., Part B*, **2**, 649 (1964).

8) K. F. Purcell and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 919 (1966).

9) K. Kawai and I. Kanesaka, *Spectrochim. Acta*, **25A**, 263 (1969).

10) R. L. Amster and R. C. Taylor, *ibid.*, **20**, 1487 (1964).

11) A. A. Woolf, *J. Chem. Soc.*, **1954**, 252.

spectra were recorded in the range from 200 to 4000 cm^{-1}. The observed frequencies are expected to be accurate within the limit of ± 5 cm^{-1} for the 4000—2000 cm^{-1} region and ± 2 cm^{-1} for the 2000—200 cm^{-1} region; their assignments are listed in Table 1, in which the two asterisked weak bands are attributable to the addition compound of hydrogen cyanide, which was present in deuterium cyanide as an impurity, with boron tribromide.

Assignments

On the basis of an examination of the structures of certain boron trihalide complexes, it seems reasonable to expect that the addition compound of hydrogen or deuterium cyanide with boron tribromide, XCN·BBr$_3$, where X is H or D, possesses the C_{3v} symmetry. Accordingly, ten normal vibrations, of which five belong to A$_1$ species and five to E species, can be expected for each compound, and all of them can be expected to be active in the infrared spectra.

In the spectra of HCN·BBr$_3$, six strong and one medium bands were observed. The two bands at 3120 and 2197 cm^{-1} are easily assigned to the C–H and C≡N stretching vibrations respectively. The isotopic shift of the ^{11}B–N and ^{10}B–N stretching frequencies is estimated to be about 30 cm^{-1} from the calculation of the normal frequencies of this type of compound. Taking account of this isotopic shift, the natural abundance of ^{11}B and ^{10}B, and the relative intensities of the observed bands, we assigned the band at 750 cm^{-1} to the ^{11}B–N stretching vibration and the weak band at 777 cm^{-1} to the ^{10}B–N stretching vibration. The isotopic shift of asymmetric ^{11}B–Br and ^{10}B–Br stretching frequencies is also estimated to be about 30 cm^{-1}; this shift has been found to be 29 cm^{-1} for (CH$_3$)$_3$N·BBr$_3$.10) Since the band at 662 cm^{-1} is too weak to assign to a normal vibration, and since this frequency was not observed in the spectra of DCN·BBr$_3$, we assigned the two bands at 674 and 696 cm^{-1} to the asymmetric ^{11}B–Br and ^{10}B–Br stretching vibrations respectively. The band at 318 cm^{-1} was assigned to both the symmetric ^{11}B–Br and ^{10}B–Br stretching vibrations, and the medium band at 363 cm^{-1}, to C≡N–B bending vibration. In addition to those bands, several weak bands were observed. The two bands at 795 and 207 cm^{-1} may be assigned to the H–C≡N and N–B–Br bending vibrations respectively. The remaining weak bands were assigned as combination or overtone bands, for which we propose two normal frequencies, 188 and 150 cm^{-1}.

The bands observed in the spectra of DCN·BBr$_3$ were assigned by comparing their frequencies with those assigned to the normal vibrations of HCN·BBr$_3$ or DCN·BCl$_3$.1) The two strong bands at 2594 and 1942 cm^{-1} and the medium band at 656 cm^{-1} are easily attributable to the coordinated DCN group. From the tentative assignment of the weak bands as combination or overtone bands, three normal frequencies were proposed, as is shown in Table 1.

The normal frequencies thus assigned for four isotopic compounds, HCN·^{10}BBr$_3$, HCN·^{11}BBr$_3$, DCN·^{10}BBr$_3$, and DCN·^{11}BBr$_3$, are listed in Table 2.

Table 2. The normal frequencies of XCN·BBr$_3$a) (cm^{-1})

Species	Mode	HCN·^{10}BBr$_3$	HCN·^{11}BBr$_3$	DCN·^{10}BBr$_3$	DCN·^{11}BBr$_3$
A_1	ν_1 ν(C–X)a)	3120	3120	2594	2594
	ν_2 ν(C≡N)	2197	2197	1942	1942
	ν_3 ν(N–B)	777	750	776	749
	ν_4 ν(B–Br)	318	318	317	317
	ν_5 δ(NBBr)	207	207	198	198
E	ν_6 δ(XCN)a)	795	795	656	656
	ν_7 ν(B–Br)	696	674	696	674
	ν_8 δ(CNB)	363	363	350	350
	ν_9 δ(NBBr)	188	188	174	174
	$\nu_{10}$$\delta$(BrBBr)	150	150	150	150

a) X=H or D.

Normal Coordinate Analysis

In order to confirm the assignment of the observed frequencies and calculate the force constants, a normal coordinate analysis was carried out for the four isotopic compounds on the assumption of a modified Urey-Bradley force field which contains two bending-bending interaction constants, I[CNB,NBBr] and I[HCN,CNB] or I[DCN,CNB].

The interatomic distances were assumed to be B–Br= 1.95, N–B=1.56, C≡N=1.16, and C–H or C–D= 1.07 Å, and the valence angle was assumed to be tetrahedral for the NBBr$_3$ group.

Since the harmonic oscillator approximation was applied in this analysis, the C–H and C≡N stretching force constants of the addition compounds of hydrogen cyanide, K[C–H] and K[C≡N], were expected to be considerably different from the C–D and C≡N stretching force constants of the addition compounds of deuterium cyanide, K[C–D] and K[C≡N], as has been found for free hydrogen and deuterium cyanides or the addition compounds of those cyanides.2) It may probably be assumed that the same values of force constants can be applied to the addition compounds with boron ten and those with boron eleven, and that F' (linear repulsive force constant) is $-0.1F$ (repulsive force constant) as usual. Accordingly, fourteen force constants were calculated from the normal frequencies listed in Table 2 by the least-squares method.

The numerical calculation was carried out by means of a computer program reported previously,12) using an electronic computer HITAC 5020E, at the Computer Center of The University of Tokyo. The calculated force constants are listed in Table 3, along with those of the parent compounds13) and those of the addition compounds of hydrogen and deuterium cyanides with boron trichloride, which are listed for the sake of comparison. The mean deviation of the calculated frequencies from the observed ones is 2.4 cm^{-1}, while the largest is 6.9 cm^{-1}.

The potential energy distributions (PED), defined as $(\mathrm{PED})_{ij}=(L_{ij})^2\times(F_s)_{ii}/\lambda_j\times 100$, where λ_j is the jth

---

12) T. Shimanouchi, "Computer Program, BGLZ and LSMB," The University of Tokyo (1968).

13) K. Shimizu and H. Shingu, *Spectrochim. Acta*, **22**, 199 (1966).

Table 3. The force constants of $HCN\cdot BBr_3$, $DCN\cdot BBr_3$, $HCN\cdot BCl_3$, $DCN\cdot BCl_3$, BBr_3, HCN, and DCN (mdyne/Å)

	$HCN\cdot BBr_3$ & $DCN\cdot BBr_3$	$HCN\cdot BCl_3$[2] & $DCN\cdot BCl_3$	BBr_3[13]	HCN[b]	DCN[b]
K[C–H]	5.094	5.229		5.817	
K[C–D]	5.790	5.876			6.058
K[C≡N]^h	19.480	19.193		18.019	
K[C≡N]^d	17.698	17.680			17.721
K[N–B]	1.710	1.581			
K[B–X][a]	1.193	1.601	2.397		
H[H(D)CN]	0.261	0.241		0.261	0.247
H[CNB]	0.289	0.233			
H[NBX][a]	0.269	0.179			
H[XBX][a]	0.124	0.151	0.058		
F[X··X][a]	0.406	0.444	0.422		
F[N··X][a]	0.397	0.613			
I[CNB,NBX][a]	0.363	0.213			
I[H(D)CN,CNB]	0.040	0.050			

a) X is Br or Cl. b) The force constants calculated from the normal frequencies listed in reference 14. h or d refers to HCN or DCN, respectively.

Table 4. The potential energy distributions for $HCN\cdot {}^{10}BBr_3$

Species A_1	Calculated frequencies				
	3120	2197	780	321	203
C–H str.	91.19	8.73	0.05	0.03	0.00
C≡N str.	8.74	88.06	1.75	1.35	0.10
N–B str.	0.07	3.31	81.71	20.97	3.41
B–Br sym. str.	0.00	0.00	22.46	43.42	41.82
BrBBr sym. bend.	0.00	0.01	41.79	23.25	42.55

Species E	Calculated frequencies				
	800	700	368	185	150
B–Br asym. str.	0.10	81.06	12.78	15.13	4.05
NBBr asym. bend.	0.44	53.50	29.72	35.76	10.60
BrBBr asym. bend.	0.03	25.12	2.31	1.66	77.74
CNB bend.	5.87	13.91	91.41	15.05	0.25
HCN bend.	102.02	0.16	0.43	0.08	0.02

Table 5. The potential energy distributions for $HCN\cdot {}^{11}BBr$

Species A_1	Calculated frequencies				
	3120	2197	749	320	202
C–H str.	91.19	8.73	0.05	0.03	0.00
C≡N str.	8.74	88.09	1.76	1.32	0.10
N–B str.	0.07	3.27	82.85	19.93	3.35
B–Br sym. str.	0.00	0.00	21.97	44.50	41.23
BrBBr sym. bend.	0.00	0.01	40.73	23.72	43.14

Species E	Calculated frequencies				
	800	670	368	185	150
B–Br asym. str.	0.05	80.62	13.47	14.99	4.00
NBBr asym. bend.	0.54	54.17	28.92	35.91	10.49
BrBBr asym. bend.	0.01	24.79	2.45	1.65	77.95
CNB bend.	6.03	14.50	90.65	15.05	0.24
HCN bend.	102.09	0.08	0.43	0.08	0.02

Table 6. The potential energy distributions for $DCN\cdot {}^{10}BBr_3$

Species A_1	Calculated frequencies				
	2594	1942	777	316	202
C–D str.	65.45	34.27	0.17	0.11	0.01
C≡N str.	34.01	62.11	2.14	1.62	0.13
N–B str.	0.55	3.77	80.35	21.14	3.66
B–Br sym. str.	0.00	0.01	22.81	44.01	40.88
BrBBr sym. bend.	0.00	0.02	42.38	38.03	43.17

Species E	Calculated frequencies				
	701	649	344	176	149
B–Br asym. str.	80.41	1.30	13.92	14.50	3.00
NBBr asym. bend.	54.06	0.69	34.17	27.73	13.38
BrBBr asym. bend.	24.92	0.37	2.26	4.71	74.59
CNB bend.	15.12	15.26	76.07	19.01	1.01
DCN bend.	0.77	96.27	4.67	0.85	0.41

Table 7. The potential energy distributions for $DCN\cdot {}^{11}BBr_3$

Species A_1	Calculated frequencies				
	2594	1942	746	315	202
C–D str.	65.46	34.27	0.17	0.10	0.01
C≡N str.	34.01	62.16	2.13	1.58	0.13
N–B str.	0.55	3.71	81.47	20.16	3.59
B–Br sym. str.	0.00	0.01	22.35	45.05	40.30
BrBBr sym. bend.	0.00	0.01	42.36	22.46	43.75

Species E	Calculated frequencies				
	673	648	344	176	149
B–Br asym. str.	70.40	8.03	14.07	14.27	3.00
NBBr asym. bend.	58.12	0.45	34.01	27.95	13.30
BrBBr asym. bend.	22.27	2.46	2.27	4.83	74.66
CNB bend.	21.13	8.83	75.98	19.01	1.01
DCN bend.	7.38	89.55	4.67	0.85	0.14

frequency parameter, $(F_s)_{ii}$ is the ith diagonal element of the symmetry force constants, and L_{ij} is the L-matrix element, were also calculated; they are listed in Tables 4—7.

Discussion

From the values listed in Tables 4—7, it is found that the vibrational assignments listed in Table 2 are reasonable. The isotopic product ratios derived experimentally from the observed frequencies and theoretically from the masses of atoms and geometrical structure are shown in Table 8; it is also found that those four isotopic compounds obey the product rule.

In Table 9, the shifts of the C≡N stretching, C–H or C–D stretching, and H–C≡N or D–C≡N bending vibrations are summarized; they correspond to the difference between the frequencies of the parent hydrogen or deuterium cyanide,[14] that is, 2097, 3311, and 712, or 1925, 2630, and 569 cm^{-1}, and those of the

---

[14] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Van Nostrand 1962, p. 80.

TABLE 8. THE ISOTOPIC PRODUCT RATIOS IN $XCN \cdot BBr_3$[a)]

Species		Ratio	
		Obsd	Theoret
$HCN \cdot {}^{10}BBr_3/HCN \cdot {}^{11}BBr_3$	A_1	1.036	1.047
	E	1.033	1.047
$DCN \cdot {}^{10}BBr_3/DCN \cdot {}^{11}BBr_3$	A_1	1.036	1.047
	E	1.033	1.047
$HCN \cdot {}^{10}BBr_3/DCN \cdot {}^{10}BBr_3$	A_1	1.423	1.412
	E	1.358	1.356
$HCN \cdot {}^{11}BBr_3/DCN \cdot {}^{11}BBr_3$	A_1	1.429	1.412
	E	1.358	1.356

a) X=H or D.

TABLE 9. THE SHIFT OF THE FREQUENCIES OF HYDROGEN AND DEUTERIUM CYANIDES (cm^{-1})

	$\Delta\nu(C{\equiv}N)$	$\Delta\nu(C\text{–}H)$	$\Delta\delta(HCN)$
$HCN \cdot BCl_3$	92	−155	46
$HCN \cdot BBr_3$	100	−191	83
	$\Delta\nu(C{\equiv}N)$	$\Delta\nu(C\text{–}D)$	$\Delta\delta(DCN)$
$DCN \cdot BCl_3$	25	−23	42
$DCN \cdot BBr_3$	17	−36	87

addition compounds listed in Table 2 or, for the sake of comparison, those of the addition compounds with boron trichloride.[1)] From Table 9, one may notice that the shifts of the frequencies are, on the whole, more significant in the addition compounds with boron tribromide than in those with boron trichloride. This may be caused by the difference between the Lewis acidity of the boron trichloride and boron tribromide: the latter exhibits a stronger acidity than the former.[15),16)] This difference also appears in the N–B stretching force constants listed in Table 3; it is reasonably certain that the dative N–B bond in the addition compounds with boron tribromide is stronger than that in those with boron trichloride.

As has been found with regard to the force constants of the addition compounds of hydrogen and deuterium cyanides with boron trichloride,[2)] there are indications that the K[C–H] or K[C–D] of the addition compounds of hydrogen or deuterium cyanide with boron tribromide is smaller than that of free cyanides, and that the K[C≡N] of the addition compounds is slightly larger than, or nearly the same as, that of the cyanides, as is shown in Table 3. This suggests that the shift of the C≡N stretching frequency is due not only to the increase in the force constant, but also to the mechanical coupling of this vibration with the C–H or C–D stretching vibration. The appearance of the C≡N stretching frequency in the lower-frequency region in the addition compounds of deuterium cyanide with boron tribromide than in those with boron trichloride may also be explained in terms of the mechanical coupling.

The B–Br stretching force constant of the addition compounds given in Table 3 is considerably smaller than that of free boron tribromide. This indicates that the strength of the B–Br bond in the addition compounds decreases considerably as a result of the change in the hybridization from sp^2 to sp^3 at the boron atom and as a result of the increase in the polarity in the bond as well as the C–H or C–D bond of the addition compounds.

The N–^{10}B or N–^{11}B stretching frequency has been found to be 720 or 689 cm^{-1} respectively in the addition compounds of trimethylamine with boron tribromide;[10)] it seems reasonable to consider that the dative N–B bond in the addition compounds of hydrogen or deuterium cyanide is stronger than that in those of trimethylamine.

The authors wish to express their gratitude to Professor Hiromu Murata of Hiroshima University and to Dr. Isao Suzuki of The University of Tokyo for their useful suggestions.

---

15) H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.*, **78**, 2173 (1956).

16) K. Tanabe and T. Takeshita, "Acid-Base Catalysis", Sangyo Tosho 1966, p. 99.