

## Infrared Studies of Some Sensitive Vibrational Modes of Pyridines on Complex Formation with Halogens and Interhalogens

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Complexes of 2-bromopyridine, 3-chloropyridine,  $\beta$ -picoline and  $\alpha$ -picoline with halogens and interhalogens along with their positive halogen salts have been prepared and characterized. The most sensitive vibration modes have been studied in methylene chloride solution in order to see the mutual influences of donors and acceptor properties. The frequency shift in  $\text{Br}_2$ -complexes is found to be larger than that of the  $\text{I}_2$ -complexes and explained on the basis of back transfer of charge from  $\pi_g^*$ -antibonding orbital of bromine to the lowest  $\pi$ -orbital of the donors. The bonding order has been observed to be  $\text{I}_2 < \text{IBr} < \text{ICl} < \text{coordinated iodine (I)}: \text{Br}_2 < \text{BrCl} < \text{coordinated bromine (I)} \text{ and } \alpha\text{-picoline} > \beta\text{-picoline} > 3\text{-chloropyridine} > 2\text{-bromopyridine}$ .

**Key Words:** Infrared studies, Halogens, Interhalogens, Charge transfer complex.

### INTRODUCTION

The formation of charge transfer complexes is accompanied by distinct changes in the IR spectra of both the donors and the acceptors<sup>1,2</sup>. Many investigators<sup>3-5</sup> have studied the effect on the vibrational spectra of halogens but not much attention has been given to the sensitive vibrational modes of the donors. In this paper, IR spectral change on the most sensitive modes of  $\alpha$ -picoline,  $\beta$ -picoline, 2-bromopyridine and 3-chloropyridine on complex formation with the halogens has been discussed.

### EXPERIMENTAL

**Materials:**  $\alpha$ -picoline and  $\beta$ -picoline were dried over KOH and BaO for several days and distilled under reduced pressure. 2-bromopyridine (Fluka, AG), 3-chloropyridine (Aldrich Chemicals), Bromine (E. Merck),  $\text{NaClO}_4$  (BDH) and  $\text{AgNO}_3$  (AR) were used without further purifications. Iodine (BDH) was resublimed and dried over  $\text{P}_2\text{O}_5$ . ICl (E. Merck) was purified by usual method<sup>6</sup>.  $\text{CH}_2\text{Cl}_2$  (E. Merck) was dried over  $\text{CaCl}_2$  and distilled from fresh  $\text{P}_2\text{O}_5$ . IBr and BrCl were prepared<sup>6</sup>.

**Preparation of the Complexes:**  $\alpha$ -picoline and  $\beta$ -picoline compounds of  $\text{I}_2$ ,  $\text{Br}_2$ , ICl and IBr were prepared as described previously<sup>7-9</sup>.  $\alpha$ -pic-BrCl was

prepared by the addition of a saturated solution of BrCl in CCl<sub>4</sub> to a solution of  $\alpha$ -picoline in CCl<sub>4</sub> at 0°C. A light orange yellow solid appeared. It was recrystallized from pure methanol and analyzed. As bromine and bromine-chloride complexes of  $\beta$ -picoline have been found to be unstable, no attempt was made to take the spectra of solid compounds. Attempts were made to prepare solid 2-bromopy-iodine and bromine complexes but failed. Solid 2-bromopy-ICl was prepared by the addition of 2-bromopyridine in CCl<sub>4</sub> to a solution of ICl in CCl<sub>4</sub> at room temperature. It was recrystallized from alcohol and analyzed. Following similar procedure 2-bromopy-IBr and 2-bromopy-BrCl were prepared in CCl<sub>4</sub> at 0°C. But 2-bromopy-BrCl was unstable at room temperature.

3-Chloropyridine-halogen series of compounds were prepared as described previously.<sup>10</sup> In this case also solid I<sub>2</sub>, Br<sub>2</sub> and BrCl complexes could not be prepared.

**Preparation of ( $\alpha$ -pic<sub>2</sub>X)ClO<sub>4</sub>, ( $\beta$ -pic<sub>2</sub>X)ClO<sub>4</sub>, (2-bromopy<sub>2</sub>X)ClO<sub>2</sub> and (3-chloropy<sub>2</sub>X)ClO<sub>4</sub> (X = I, Br):** Bis( $\alpha$ -picoline) Silver(I) perchlorate, bis(2-bromopyridine) silver(I) perchlorate were prepared by the same method as bis(pyridine) silver(I) perchlorate<sup>11</sup>. From these compounds the respective ( $\alpha$ -pic<sub>2</sub>I)ClO<sub>4</sub>, ( $\alpha$ -pic<sub>2</sub>Br)ClO<sub>4</sub> and (2-bromopy<sub>2</sub>I)ClO<sub>4</sub> were prepared by the reported methods described in literature<sup>11-13</sup>.

**Preparation of ( $\beta$ -pic<sub>2</sub>X)ClO<sub>4</sub> and (3-chloropy<sub>2</sub>X)ClO<sub>4</sub> (X = I, Br):** A measured quantity of aqueous NaClO<sub>4</sub> was directly added to the substituted pyridines. The AgNO<sub>3</sub> solution in water was added slowly by constant stirring whereby a white solid compound was formed. It was then washed with cooled distilled water several times to remove the excess AgNO<sub>3</sub> and the solid was dried over P<sub>2</sub>O<sub>5</sub> in a desiccator. The spectral study and the estimation of silver metal indicated the compound as (substituted py<sub>2</sub>Ag)ClO<sub>4</sub>. The silver complex was dissolved in a mixture of (1 : 10) MeOH + CHCl<sub>3</sub> solution and then treated with I<sub>2</sub> or Br<sub>2</sub> solution in MeOH, whereby silver was precipitated as AgI or AgBr. It was filtered. The filtrate was treated with ether and a white compound appeared in every case. The complex was recrystallized from spectrograde methanol, dried over vacuum desiccator and analyzed.

Spectra were recorded using an IR Perkin-Elmer Model 880 in the range 1200–200 cm<sup>-1</sup>. For solutions, path-length of the cells varies from 0.02 to 0.11 mm. All the measurements were made on freshly prepared solutions. The accuracy in the wave numbers is within  $\pm 2$  cm<sup>-1</sup>. The spectral resolution in the solution was better than 1 cm<sup>-1</sup> at 2500–200 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

The band frequencies data for the most sensitive vibrations over the range 1200–200 cm<sup>-1</sup> are presented in Table-1. This table shows the spectral view of the  $\alpha$ -pic-halogen,  $\beta$ -pic-halogen, 2-bromopy-halogen, 3-chloropy-halogen and bis(pyridines<sub>2</sub>X)ClO<sub>4</sub> (X = I, Br) for the ring as well as X-sensitive modes of the donors in CH<sub>2</sub>Cl<sub>2</sub> solution and in Mulls.

TABLE-1

Compounds	m.p. (°C)	Total halogen (Calcd.)	Content % (Found)
$\alpha$ -pic-I <sub>2</sub> (dark-red)	38.5	73.2	72.5
$\alpha$ -pic-Br <sub>2</sub> (orange)	69.0	63.21	62.0
$\alpha$ -pic-ICl (yellow)	76.5	63.0	62.8
$\alpha$ -pic-IBr (orange)	66.5	68.8	68.1
$\alpha$ -pic-BrCl (orange yellow)	84	55.3	54.9
2-bromopy-ICl (yellow)	121	50.7	50.1
2-bromopy-IBr (orange)	81	56.7	56.0
2-bromopy-BrCl (orange)	Decomposed at room temperature		
3-chloropy-ICl (yellow)	56	60.0	59.2
3-chloropy-IBr (orange)	46	64.5	63.8
( $\alpha$ -pic <sub>2</sub> Br)ClO <sub>4</sub> (white)	135 d	30.8	30.75
( $\alpha$ -pic <sub>2</sub> Br)ClO <sub>4</sub> (white)	120 d	21.88	20.9
( $\beta$ -pic <sub>2</sub> I)ClO <sub>4</sub> (white)	140 d	30.8	30.7
( $\beta$ -pic <sub>2</sub> Br)ClO <sub>4</sub> (white)	135 d	21.88	21.5
(2-bromopy <sub>2</sub> I)ClO <sub>4</sub> (white)	130 d	23.4	22.9
(3-chloropy <sub>2</sub> I)ClO <sub>4</sub> (white)	142 d	27.9	27.9

The frequency shift depends upon the donor and acceptor properties of the molecules<sup>14</sup>. The relative acceptor strength depends upon their electron affinities<sup>15</sup> and it follows the trend ICl  $\gg$  BrCl > IBr > I<sub>2</sub> > Br<sub>2</sub>. So the frequency shift should be greatest in the case of *n*-donor-ICl complexes and the least for the Br<sub>2</sub>-complexes. This has been observed in the case of dioxane-halogen complexes<sup>16</sup>. But in this case a slight drift is observed. It is clear from Table-2 that the frequency shift is greater for ICl complex than for IBr which is even more for I<sub>2</sub>-complexes. It is found also to be greater for the BrCl than for the Br<sub>2</sub>-complexes. Since I<sub>2</sub> has a greater acid strength than Br<sub>2</sub>, it is expected that for all the sensitive bands, the frequency shift will be larger for I<sub>2</sub> than for Br<sub>2</sub>-complexes. But in practice exactly opposite effect is observed. A possible explanation for this anomaly may be given in terms of a back transfer of charge from  $\pi_g$ -antibonding orbital of Br<sub>2</sub> to the lowest unoccupied  $\pi$ -orbital of donors.

In CH<sub>2</sub>Cl<sub>2</sub>, all the solid complexes show a pair of bands, one of higher intensity than the other. These two bands are more pronounced in the case of  $\alpha$ -substituted pyridines. This may be due to a major change of symmetry as a result of steric hindrance. Anthonsen<sup>16</sup> has observed recently the presence of extra-bands due to lowering of symmetry as a consequence of complex formation.

The substituting groups like —CH<sub>3</sub> and halogen adjacent to the donor N-atom have some effect on the frequency shift. This is observed in both the cases of methyl and bromo-substituted pyridines in  $\alpha$ -position as the frequency shift is much higher than the  $\beta$ -substituted pyridines.

In the case of I<sub>2</sub>-complexes the shift of a particular band, e.g.,  $\nu_{\text{ring}}$  vibration

TABLE-2  
EFFECT OF THE MOST SENSITIVE VIBRATIONS OF PYRIDINES ON COMPLEX FORMATION WITH HALOGENS IN CH<sub>2</sub>Cl<sub>2</sub> AND IN MULLS

Sensitive mode <sup>17, 18</sup> of $\alpha$ -picoline	$\alpha$ -pic-I <sub>2</sub>	$\alpha$ -pic-IBr	$\alpha$ -pic-ICl	$\alpha$ -pic-BrCl	$\alpha$ -pic-Br <sub>2</sub>	( $\alpha$ -pic <sub>2</sub> )ClO <sub>4</sub>	( $\alpha$ -pic <sub>2</sub> Br)ClO <sub>4</sub>
p (ring) 999 cm <sup>-1</sup>	1014 (s), 1025 (s)	1018 (vs), 991 (s)	1020 (vs), 1008 (w)	1018 (s), 990 (w)	1016 (s), 1027 (w)	1024 (s), 999 (w)	1027 (s), 991 (w)
q (x-sen) 1102	1113 (w)	1114 (s)	1116 (vs)	1115 (s)	1114 (s)	—	—
t (x-sen) 546	548 (s)	549 (vs)	549 (vs)	550 (s)	549 (s)	550 (w)	550 (w)
Sensitive mode of 2-bromopyridine	2-bromopy-I <sub>2</sub>	2-bromopy-IBr	2-bromopy-ICl	2-bromopy-BrCl	2-bromopy-Br <sub>2</sub>	2-bromopy <sub>2</sub> ]ClO <sub>4</sub> *	
p (ring) 990	989 (s), 999 (vw)	1005 (vs), 989 (w)	1010 (w), 996 (m)	1007 (s), 990 (m)	990 (s), 1002 (w)	1013 (m)	
q (x-sen) 1109	1110 (s)	1120 (s), 1110 (m)	1122 (s), 1110 (w)	1120 (w), 1110 (s)	1110 (s)	—	
y (x-sen) 470	470 (s)	469 (w)	469 (w)	468 (w)	467 (w)	472 (m)	
s(ccc) 615	617 (s)	618 (vw), 626 (s)	631 (s)	630 (s), 614 (w)	625 (m), 614 (s)	635 (m)	
Sensitive mode of 3-chloropyridine	3-chloropy-I <sub>2</sub>	3-chloropy-IBr	3-chloropy-ICl	3-chloropy-Br <sub>2</sub>	3-chloropy <sub>2</sub> ] ClO <sub>4</sub> *		
p (ring) 1014	1020 (s)	1029 (w), 1018 (w)	1030 (m), 1019 (vw)	1025 (vw), 1019 (s)	1027 (w)		
v (cc) 693	702 (w)	687 (w)	688 (w)	701 (w)	682 (s)		
Sensitive mode of $\beta$ -picoline	$\beta$ -pic-I <sub>2</sub>	$\beta$ -pic-IBr	$\beta$ -pic-ICl	$\beta$ -pic-BrCl	$\beta$ -pic-Br <sub>2</sub>	( $\beta$ -pic <sub>2</sub> ) ClO <sub>4</sub>	( $\beta$ -pic <sub>2</sub> Br)ClO <sub>4</sub>
p (ring) 1044	1058 (s), 1055 (s)	1061 (s)	1064 (m)	1065 (s), 1042 (w)	1060 (s)	1064 (m)	
y (x-sen) 629	652 (m), 645 (s)	655 (s), 650 (w)	652 (s), 650 (w)	653 (w), 632 (w)	653 (w), 650 (s)	647 (w)	654 (s)

\*Spectra are taken in Mull.

is the lowest and for co-ordinated complex it is the highest. This trend is observed for all other sensitive modes. From these observations, we have come to the conclusion that the strengths of the complexes are in the order: coordinated Iodine (I) > ICl > IBr > I<sub>2</sub> and co-ordinated bromine (Br) > BrCl > Br<sub>2</sub>.

From the foregoing observations it is obvious that the frequency shift depends upon the following factors:

- (i)  $\sigma$ -bonding lone pair donation from nitrogen to halogen.
- (ii) Back donation from halogen to ring.
- (iii) Steric effect due to the presence of substituent groups in the donor molecules.
- (iv) Change of symmetry.
- (v) Charge transfer from filled  $\pi$ -orbital of the ring to the vacant d-orbital of the halogen.

### REFERENCES

1. D.L. Glusker and H.W. Thomson, *J. Chem. Soc.*, 471 (1955).
2. R.A. Zingaro and W.B. Witmer, *J. Phys. Chem.*, **64**, 1705 (1960).
3. R.S. Mulliken and W.B. Person, *Molecular Complexes: A Lecture and Reprint Volume*, Wiley-Interscience, New York (1969).
4. R. Foster, *Organic Charge-Transfer Complexes*, Academic Press, New York (1969).
5. E.N. Guryanova, I.P. Goldshtein and I.P. Romm, *Donor Acceptor Bond*, John Wiley, New York (1975).
6. J. Cornog and R.H. Karges, *Inorg. Synth.*, **1**, 165 (1939).
7. A.I. Popov and R.H. Rygg, *J. Am. Chem. Soc.*, **79**, 4622 (1957).
8. J.P. Saxena and M.P. Gelra, *Indian J. Chem. Soc.*, **6**, 562 (1968).
9. S.K. Baruah and I. Haque, *J. Indian Chem. Soc.*, **63**, 490 (1986).
10. M.T. Rogers and W.K. Mayer, *J. Phys. Chem.*, **66**, 1397 (1962).
11. *Inorg. Synth.*, **7**, 169 (1963).
12. R.A. Zingaro, C.A. Vanderwerf and J. Kleinberg, *J. Am. Chem. Soc.*, **71**, 575 (1949).
13. I. Haque and J.L. Wood, *J. Mol. Struct.*, **2**, 217 (1968).
14. ———, *Spectrochim. Acta*, **23A**, 259 (1967).
15. ———, *Spectrochim. Acta*, **23A**, 2523 (1967).
16. J.W. Anthonsen, *Spectrochim. Acta*, **32A**, 963 (1976).
17. E. Spinner, *J. Chem. Soc.*, 3860 (1963).
18. A.H. Shafy, H. Perlmatter and H. Kimmel, *J. Mol. Struct.*, **42**, 37 (1977).

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