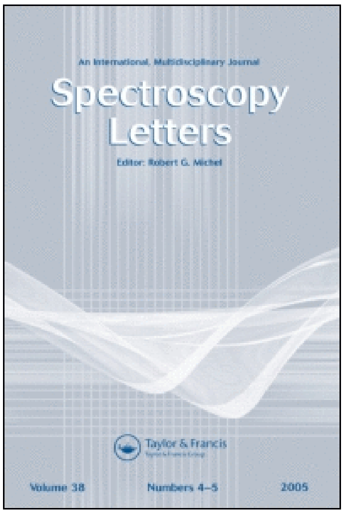

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# Mechanochemical Reaction Between the Probe and the Matrix: A Possible Source of Errors When IR Spectra of Alkali Acid Bifluorides Are Recorded in Alkali Halide Pressed Disks

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## ABSTRACT

The mechano-chemical reactions of alkali acid bifluorides ($MHF_2$), with alkali halides (MX), were studied by x-ray diffraction (XRD) and IR spectroscopy. The reactions were carried out by milling the solid reagents in equimolar ratio by hand in an agate mortar. $LiHF_2$ is unstable on milling and decomposes to LiF and HF. Rb, Cs, and $NH_4$ acid bifluorides react

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with KBr leading to the corresponding bromides and stable $KHF_2$. Similar reactions are observed with Na halides, leading to $NaHF_2$. $NaHF_2$ reacts with KF to form $KHF_2$ and NaF. The mechano-chemical reactions with alkali halides are considered in connection with the use of alkali halides as matrices for IR spectroscopy.

*Key Words:* Acid bifluorides; Alkali halides; IR spectroscopy; X-ray diffraction; Mechanochemistry.

## INTRODUCTION

IR spectroscopy is a powerful technique for the study of solid, liquid, and gaseous samples. The IR spectra of solid samples are usually recorded by dispersing the probe in an alkali halide matrix, through a milling process, and then pressing the mixture to obtain a thin disk appropriate for the experiment. However, in this preparative process the nature of the probe can be altered through a mechano-chemical reaction with the matrix.[1] For substances which can react with the alkali halide matrix, for example, silver compounds, the probe is usually dispersed in Nujol, although in this case also a reaction with the windows could be present.[2]

Alkali fluorides are basic salts that can abstract a proton from acidic substances in the solid state leading to the very stable acid bifluoride salts.[3,4] We have studied these reactions in the solid state using IR spectra to monitor the processes.[3,4] However, the acid bifluorides are very reactive, hygroscopic species which can interact with the alkali halide matrices of the pressed disks used in IR spectroscopy. Ketelaar et al.[5] have noticed that the IR spectra of the bifluoride anion depend on the nature of the matrix used in the determination of the spectra, which has been interpreted as formation of mixed crystals where the $(FHF)^-$ ion is enclosed in the alkali halide lattice to form a solid solution. However, due to the high dilution of the acidic bifluoride in the matrix used in IR spectroscopy, it is difficult to determine the nature of the process without an exhaustive study of the involved mechano-chemical reactions.

In this paper we present our x-ray diffraction (XRD) and IR results of equimolar mixtures of alkali acid bifluorides and alkali halides, milled in an agate mortar. We are not aware of published results on these mechanochemical reactions, which are relevant in the study of acid bifluorides, by IR spectroscopy using the alkali halide pressed disk technique.

## EXPERIMENTAL

The alkali acid bifluorides ($LiHF_2$, $NaHF_2$, $KHF_2$, $RbHF_2$, $CsHF_2$) and $NH_4HF_2$ were prepared from the corresponding fluorides by adding an excess of HF and then allowing the nonreacted HF to evaporate. The products were then purified by recrystallization to eliminate traces of the starting reagents. Their nature was established by IR spectroscopy, in Nujol mull, and XRD by comparison with the corresponding reported patterns.[4] All the reagents used were analytical grade chemicals from Sigma or Merck.

The milling process of the alkali acid bifluoride and alkali halide mixtures was carried out by hand in an agate mortar for several minutes. The milled mixtures were then studied by XRD and IR techniques. XRD powder patterns were recorded in a D8 Advance diffractometer (Bruker) using CuK$_\alpha$ radiation. IR spectra were run in Nujol mulls, and on thin pressed disks of the equimolar milled mixtures, using an FT-IR spectrophotometer (Equinox 55 from Bruker). The absorption bands of the $(FHF)^-$ anion were assigned according to the vibrational spectra calculated by Epa and Thorson[6,7] for this specie.

Also, the XRD study was done on a set of samples with a slight excess of the acidic species ($MHF_2$) in order to evaluate the converted fraction (CF) for a given milling time from the intensity ratio of the most intense reflection of the involved alkali halides:

$$\frac{CF = I_{100}(MBr_{Formed})}{I_{100}(KBr) + I_{100}(MBr_{Formed})} \tag{1}$$

## RESULTS AND DISCUSSION

When equimolar mixtures of $RbHF_2$, $CsHF_2$, and $NH_4HF_2$ with $K^+$ halides are milled, reaction products $KHF_2$ and $Rb^+$, $Cs^+$ and $NH_4^+$ halides are obtained. Figure 1 shows the XRD powder patterns of the corresponding milled mixtures with KBr, where the formation of CsBr, RbBr, $NH_4Br$, and $KHF_2$ are observed, according to the reactions:

$$CsHF_2 + KBr \longrightarrow KHF_2 + CsBr \tag{2}$$

$$RbHF_2 + KBr \longrightarrow KHF_2 + RbBr \tag{3}$$

$$NH_4HF_2 + KBr \longrightarrow KHF_2 + NH_4Br \tag{4}$$

An analogous result is obtained when $RbHF_2$, $CsHF_2$, and $NH_4HF_2$ are milled with $Na^+$ halides where $NaHF_2$ is the acidic species formed:

$$CsHF_2 + NaX \longrightarrow NaHF_2 + CsX \tag{5}$$

$$RbHF_2 + NaX \longrightarrow NaHF_2 + RbX \tag{6}$$

$$NH_4HF_2 + NaX \longrightarrow NaHF_2 + NH_4X \tag{7}$$

where $X = Cl^-, Br^-, I^-$.

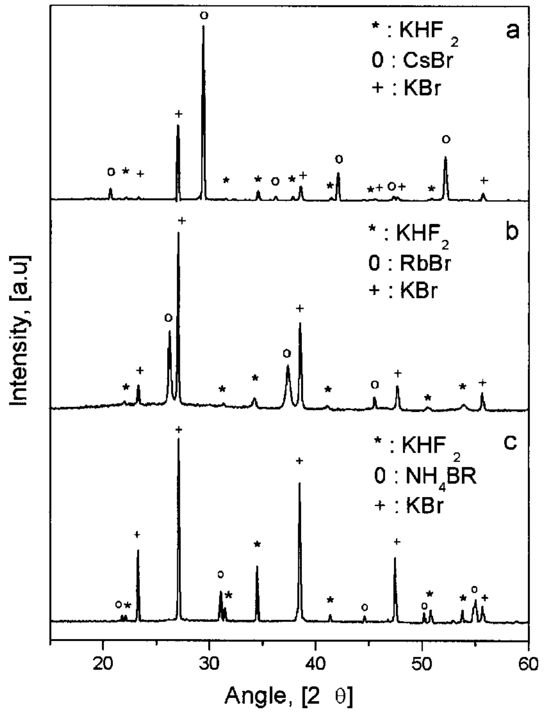

*Figure 1.* XRD powder patterns corresponding to the milled mixtures of: (a) $CsHF_2 + KBr \rightarrow CsBr + KHF_2$; (b) $RbHF_2 + KBr \rightarrow RbBr + KHF_2$; (c) $NH_4HF_2 + KBr \rightarrow NH_4Br + KHF_2$. These XRD powder patterns were recorded on samples after 2 min of milling and with an excess of KBr in order to favor a complete reaction with the acidic bifluorides.

The driving force for these double decomposition reactions must be the higher stability of $NaHF_2$ and $KHF_2$ compared with their analogs of $Rb^+$, $Cs^+$, and $NH_4^+$. The compound $KHF_2$ also undergoes a similar reaction when milled with the Na halides except for NaF [see Fig. 2(a) and (b)]:

$$KHF_2 + NaX \longrightarrow NaHF_2 + KX \qquad (8)$$

where $X = Cl^-, Br^-, I^-$. This suggests that $NaHF_2$ is more stable than $KHF_2$.

During the milling of mixtures of $NaHF_2$, $KHF_2$, $RbHF_2$, $CsHF_2$, and $NH_4HF_2$, with Li halides, the evolution of HF can be detected as a penetrating acidic odor. In the corresponding XRD powder patterns, LiF and $Na^+$, $K^+$,

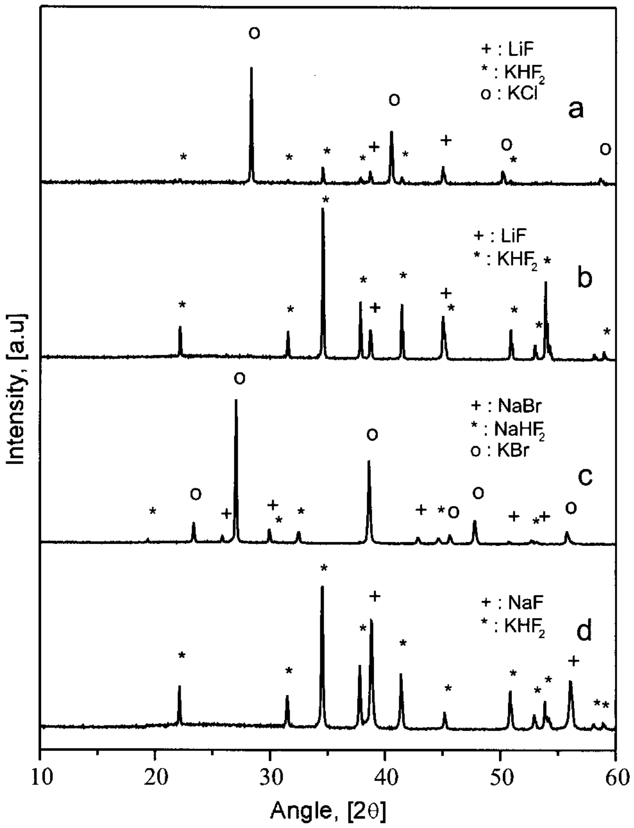

***Figure 2.*** XRD powder patterns corresponding to the milled mixtures of: (a) $KHF_2 + LiCl \rightarrow KCl + LiF + HF$ ($KHF_2$ in excess); (b) $KHF_2 + LiF$ (no reaction was observed); (c) $KHF_2 + NaBr \rightarrow KBr + NaHF_2$ (NaBr in excess); (d) $KHF_2 + NaF$ (no reaction was observed).

$Rb^+$, $Cs^+$, and $NH_4^+$ halides are always detected [see Fig. 2(c) and (d)], according to:

$$MHF_2 + LiX \longrightarrow LiF + HF + MX \tag{9}$$

where $M = Na^+, K^+, Rb^+, Cs^+$, and $NH_4^+$; and $X = Cl^-, Br^-, I^-$.

On milling, the ionic exchange reactions in mixtures of alkali acid bifluorides with alkali halides proceed according to the following order:

$$NaHF_2 > KHF_2 > RbHF_2 > NH_4HF_2 > CsHF_2 \tag{10}$$

which parallels the order of "acidity" of the involved cations ($Na^+ > K^+ > Rb^+ > H_4^+ > Cs^+$).

LiF is totally inert when milled with acid bifluoride, due to the high stability of the salt. When $LiHF_2$ was milled, without a second component, it decomposed giving LiF and HF. It seems that the small ionic radii of $Li^+$ and $F^-$ favors a higher stability of LiF when compared with the acidic species. According to this point of view, the following alkali fluoride in order of stability must be NaF and probably this explains the reaction of $NaHF_2$ with KF in favor of $KHF_2$ formation:

$$NaHF_2 + KF \longrightarrow KHF_2 + NaF \tag{11}$$

After some minutes of milling in an agate mortar, $NaHF_2$ also decomposes to give NaF + HF. The milling process shows an equivalence with heating. During the milling the contact points of the colliding microcrystals behave as hot points where certain thermochemical reactions take place.[8] On heating $LiHF_2$ and $NaHF_2$ decompose to form the highly stable fluorides, LiF and NaF, plus HF.

The above-discussed mechano-chemical reactions take place in relatively short milling times. Figure 3 shows the dependence of the converted fraction for given milling time, estimated according to Eq. (1), for the reactions of $CsHF_2$, $RbHF_2$, and $NH_4HF_2$ with KBr. These are relatively fast reactions, which take place within the range of time usually employed in the milling and pressing process during the disk preparation for IR spectroscopy. The reaction rate parallels the order of hygroscopicity of the acidic species involved,

$$CsHF_2 > RbHF_2 > NH_4HF_2 \tag{12}$$

The IR-allowed vibrations, $\nu_2$ and $\nu_3$, and their combinations with $\nu_1$ (IR forbidden) from the $(FHF)^-$ anion are sensible to the accompanied cation. In Table 1 are collected the frequencies for $\nu_2$, $\nu_3$, $(\nu_1 + \nu_2)$, and $(\nu_1 + \nu_3)$ from IR spectra recorded on thin pressed disks of the equimolar milled mixtures. These IR results are in accordance with those discussed above from XRD.

The ionic exchange and decomposition reactions discussed above, when present during the alkali halide disk preparation for IR spectroscopy, change the nature of the studied acid bifluoride sample. An examination of published IR spectra of acid bifluorides, in alkali halide pressed disk,[4] reveals the

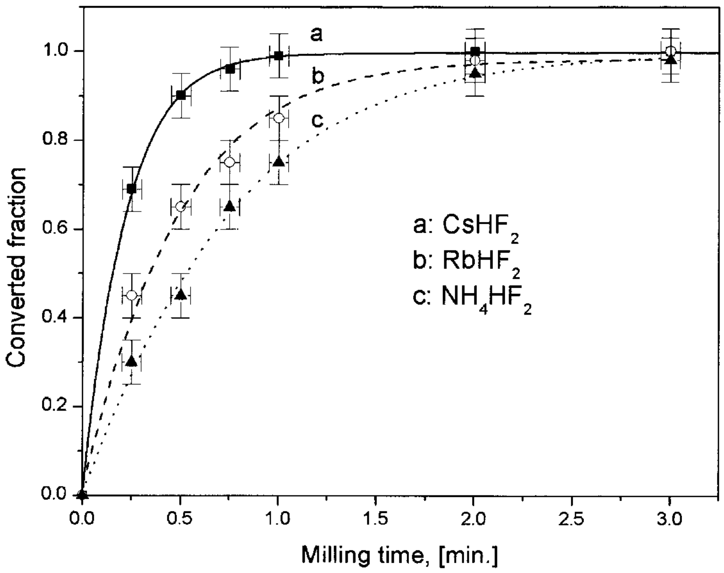

***Figure 3.*** CF for the mechano-chemical reaction between $CsHF_2$, $RbHF_2$, and $NH_4HF_2$ with KBr to form $KHF_2$ and the corresponding alkali bromide (MBr). The CF values were estimated according to Eq. (1).

***Table 1.*** IR absorption bands of some alkali acid bifluorides in alkali halide matrices.

| | Frequency of the main IR absorption bands | | | |
|---|---|---|---|---|
| Sample/disk matrix | $\nu_2$ | $\nu_3$ | $\nu_1 + \nu_2$ | $\nu_1 + \nu_3$ |
| $KHF_2$/KBr | 1,257 | 1,525 | 1,839 | 2,103 |
| $NaHF_2$/NaBr | 1,245 | 1,595 | 1,830 | 2,131 |
| $KHF_2$/NaBr | 1,257 | 1,525 | 1,839 | 2,103 |
| $NaHF_2$/KBr | 1,256 | 1,525 | 1,838 | 2,104 |
| $RbHF_2$/CsBr | 1,246 | 1,488 | 1,832 | 2,060 |
| $RbHF_2$/KBr | 1,257 | 1,521 | 1,830 | 2,098 |
| $CsHF_2$/CsBr | 1,245 | 1,485 | 1,829 | 2,064 |
| $CsHF_2$/KBr | 1,256 | 1,512 | 1,859 | 2,101 |
| $NH_4HF_2$/CsBr | 1,247 | 1,490 | 1,833 | 2,113 |
| $NH_4HF_2$/KBr | 1,256 | 1,524 | 1,840 | 2,100 |

*Note*: All these spectra were recorded on thin disks of the equimolar milled mixtures.

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occurrence of a sample–matrix interaction that changes the nature of the former one.

## CONCLUSIONS

When a mixture of an alkali acid bifluoride and an alkali halide are milled, an ionic exchange reaction takes place to form the most stable system. The reaction of $Cs^+$, $Rb^+$, and $NH_4^+$ acid bifluorides with KBr leads to the formation of CsBr, RbBr, and $NH_4Br$, and $KHF_2$. With $Na^+$ halides, the products are the corresponding halides plus $NaHF_2$. The higher stability of $NaHF_2$ and $KHF_2$ is the driving force for these reactions. $KHF_2$ reacts with $Na^+$ halides to form $NaHF_2$ except NaF. However, $NaHF_2$ reacts with KF leading to $KHF_2$ and NaF. Undoubtedly, the stability of NaF determines this reaction. $LiHF_2$ is unstable on milling to give LiF and HF. LiF does not react with acid bifluorides to form $LiHF_2$. The occurrence of these ionic exchange and decomposition reactions need to be considered to avoid errors in the study of $MHF_2$ by IR spectroscopy.

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