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Mechanochemical reactions of telluric acid with alkaline fluorides

José Fernández-Bertran[a], Edilso Reguera[b], Armando Paneque[a],
Hernani Yee-Madeira[c,*], Alvaro Gordillo-Sol[c]

[a]*Center of Pharmaceutical Chemistry, Havana, Cuba*
[b]*Institute of Materials and Reagents, Havana University, Havana, Cuba*
[c]*Escuela Superior de Física y Matemáticas-IPN, Edif. 9 U.P. "ALM" Col. Lindavista, 07738 México, D.F., México*

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Abstract

The mechanochemical reactions of telluric acid, $Te(OH)_6$ with alkaline fluorides (Na and K) have been studied using IR and XRD techniques. The reactions lead to the formation of hydrogen-bonding complexes, $NaF.Te(OH)_6$ and $2KF.Te(OH)_6$. The reactions are free from side products such as alkali tellurates, alkali fluorotellurates or HF_2^- salts. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ionic fluorides are widely used as basic reagents in organic chemistry [1] and fluoride ion affinities provide a novel scale for Lewis acidities [2]. With Brönsted acids the fluoride anion is capable of subtracting a proton, forming the very stable acid difluoride anion HF_2^- [3]. In the solid state, even weak acids such as nicotinic ($K_a = 1.4 \times 10^{-5}$) react mechanochemically with KF to form K nicotinate and KHF_2 [4].

$$2KF + RCO_2H \rightarrow RCO_2K + KHF_2 \qquad (1)$$

Telluric acid, $Te(OH)_6$, is a very weak Brönsted acid ($K_{a1} = 2.09 \times 10^{-9}, K_{a2} = 6.46 \times 10^{-12}$). Its reactions with soluble fluorides have been studied in water solutions. With aqueous HF, the reaction leads to the successive substitution of $(OH)^-$ groups by F^-, forming the whole series of fluorotelluric acids $Te(OH)_{6-x}F_x$ up to TeF_6 [5]. The hexafluoride can be hydrolyzed slowly in water giving the fluorotelluric acids in reverse order down to $Te(OH)_6$ [6].

A water solution of telluric acid can react with solutions of NaF and KF giving crystalline complexes in which the F^- anion is hydrogen-bonded to three hydroxyl protons [7,8]. The stoichiometries are $NaF{\cdot}Te(OH)_6$ and $2KF{\cdot}Te(OH)_6$.

The reactions of telluric acid with alkali fluorides in the solid state have not been reported. Three different courses for the mechanochemical reactions can be envisaged.

1. Formation of the hydrogen bonding (HB) complexes as in water solution [7,8].
2. Subtraction of acidic protons with formation of acid difluoride alkali salts and alkali tellurates [4].
3. Ligand substitution of $(OH)^-$ for F^- leading to fluorotelluric acids or the alkaline salts.

We have performed mechanochemical reactions of crystalline telluric acid with solid NaF and KF in an agate mortar, monitoring the reactions by XRD and IR techniques. The results indicate an efficient reaction of type 1 with no side products, leading to the HB complexes.

2. Experimental

The chemicals telluric acid, NaF and KF were analytical grade reagents from BDH and SIGMA. The milling of telluric acid with alkaline halides in proper molecular ratios was carried out by hand in an agate mortar for 10–20 m. The milled paste was left to stand in desiccators at 50 °C.

The samples were analyzed by XRD and IR using a D-8 advance diffractometer (from Bruker) and an Equinox 55 FTIR spectrophotometer (also from Bruker), respectively. The IR spectra were run in KBr pressed disks, milling first the KBr and gently milling the sample with the matrix to avoid mechanochemical reactions [4].

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[*] Corresponding author. COFAA-Fellow. Tel.: +52-5729-6000; fax: +52-5729-55049.
E-mail address: yee@esfm.ipn.mx (H. Yee-Madeira).

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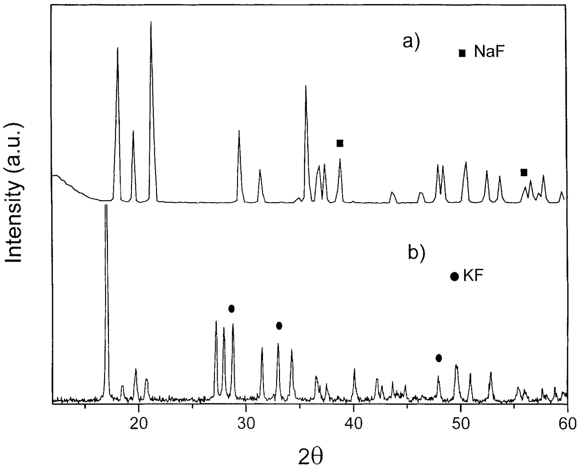

Fig. 1. XRD powder patterns of: (a) NaF·Te(OH)$_6$ obtained from the mechanochemical reaction of NaF and Te(OH)$_6$ in 1:1 molar ratio; (b) 2KF·Te(OH)$_6$ obtained from the mechanochemical reaction of KF and Te(OH)$_6$ in a 2:1 molar ratio.

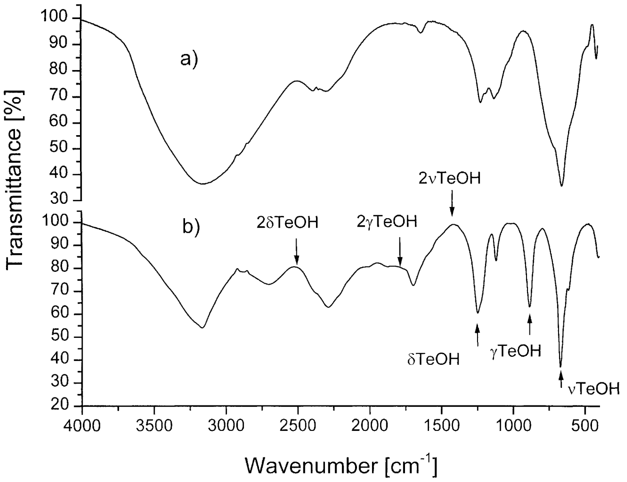

Fig. 2. IR spectra of: (a) Telluric acid, Te(OH)$_6$; (b) NaF·Te(OH)$_6$ obtained from the mechanochemical reaction of NaF and Te(OH)$_6$ in a 1:1 molar ratio.

3. Results and discussion

3.1. XRD results

The method of XRD proved powerful in identifying the reaction products. Milling equimolar amounts of NaF and Te(OH)$_6$ lead to a paste, which was not hygroscopic. The diffraction peaks of the crystalline complex NaF.-Te(OH)$_6$ [8] are the only reflections in the XRD pattern (Fig. 1a). The reaction is fast and complete and no side products are observed. If the molar ratios of the reagents are different from 1:1, excess of one of the reagents is observed.

When KF and Te(OH)$_6$ are milled in a 2:1 molar ratio, a paste is first formed which hardens in a few minutes. The XRD pattern shown in Fig. 1b, corresponds to the crystalline complex 2KF.Te(OH)$_6$. Again in this case the reaction is fast and clean. If a 1:1 molar ratio is used, excess of telluric acid occurs.

3.2. Infrared results

Infrared spectra are important in studying the characteristic of HB complexes [9–12]. Hadzil [9] recognizes three types of spectra:

1. Weak interactions in which the ν_{OH} band shifts are small.
2. Stronger hydrogen bonds, which give a broad band from 3000 to 1600 cm^{-1} corresponding to a displaced ν_{OH}.
3. Very strong hydrogen bonds, which give a broad band below 1600 cm^{-1}, called the D band, which presents narrow windows [11,12].

The IR spectra of telluric acid in KBr disk is typical of the second class corresponding to strong hydrogen bonds. (Fig. 2a).

On milling telluric acid with NaF, the spectrum changes as can be seen in Fig. 2b. There are small displacements in the low frequency fundamentals bellow 1500 cm^{-1}, δ_{TeOH}, γ_{TeOH} and ν_{TeOH}. The assignments are those of Allman [8]. However, in the high frequency region the broad OH band of telluric acid in the 3700–1700 cm^{-1} region, has shifted almost down to 1500 cm^{-1} and a series of gaps, called Evans windows divide the broad absorption [11,12]. This windows are produce by Fermi resonance interactions of ν_{OH} with the harmonics of δ_{TeOH}, γ_{TeOH} and ν_{TeO}. (Fig. 2b). The interactions repel the ν_{OH} absorption from the position of the harmonics, which are at the minimum absorption frequencies. In NaF.Te(OH)$_6$ three OH groups are bound to the F$^-$ anion through strong HB while three other OH$^-$ groups interact among themselves as in telluric acid. We interpret the strong band at 3165 cm^{-1} as corresponding to the OH → OH interactions in accordance with Allman [7]. The OH → F vibrations comprise the broad absorption from 3000 to 1500 cm^{-1}, gaped by Fermi resonance interactions. (Fig. 2b). It is surprising that the OH–F interactions does not produce a spectra of type 3. The most probable explanation is that the saturation of F$^-$ by three hydrogen bonds weakens the effect, which is greater for a single OH–F bond [13].

The IR spectra of 2KF·Te(OH)$_6$ in KBr are analogous to those in Nujol mull obtained by Allman [8]. This indicates that the gentle milling of the complex with KBr does not disrupt it [14,15]. In none of the spectra the absorption lines of the HF$_2$$^-$ anion were detected, in accordance with XRD results [16,17].

4. Conclusions

The milling of telluric acid with NaF and KF leads to crystalline HB complexes of stoichiometry NaF.Te(OH)$_6$ and 2KF.Te(OH)$_6$. These complexes can also be obtained from crystallization in water or methanolic solutions of the reagents. In spite of the short O–F distance in the Na and K complexes, the HB are not of the very strong type according to IR. Perhaps the saturation of F^- by three OH bonds weakens them in relation to the simple OH–F bond. Telluric acid does not behaves mechanochemically as a Brönsted or Lewis acid The presence of the acid difluoride anion is not detected indicating that the fluorides used are not capable of subtracting protons from the weak telluric acid. No substitution of OH^- by F^- is observed. The mechanochemical process is very efficient and clear in the production of the HB complexes, without any side products from other reactions.

References

[1] J.A. Clark, Chem. Rev. (1980) 429–452.

[2] K.O. Christe, D.A. Dixon, D. Mc Hemore, W.W. Wilson, J.A. Sheehy, J.A. Boatz, J. Fluorine Chem. 101 (2000) 151–153.

[3] G.C. Pimentel, J. Chem. Phys. 19 (1951) 446.

[4] J. Fernandez-Bertran, E. Reguera, Solid State Ion. 112 (1998) 351–354.

[5] U. Elgad, H. Selig, J.C.S. Chem. Comm. 14 (1975) 140–145.

[6] G.W. Fraser, G.D. Meikle, J. C. S. Chem. Comm. (1974) 624–625.

[7] R. Allman, Acta Crystallogr. B 32 (1976) 1025.

[8] R. Allman, W. Haase, Inorg. Chem. 15 (1976) 804–807.

[9] D. Hadzc, Pure Appl. Chem. 11 (1965) 435.

[10] M.F. Claydon, N. Sheppard. Chem. Comm. (1969) 1431.

[11] J.C. Evans, Spectrochim. Acta 17 (1961) 129.

[12] J.C. Evans, Spectrochim. Acta 18 (1962) 507.

[13] J. Emsley, Chem. Soc. Rev. 9 (1980) 91.

[14] A. Valor, J. Fernandez-Bertran, J. Radilla, J. Fluorine Chem. 107 (2001) 137–139.

[15] J. Fernandez-Bertran, E. Reguera, Solid State Ionics 93 (1997) 139.

[16] G.L. Cote, H.W. Thompson, Proc. Roy. Soc. 210 (1951) 206.

[17] J.L. Jones, R.A. Penneman, J. Chem. Phys. 22 (1954) 781.