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Rotational studies of adducts between carboxylic acids and tertiary alcohols: Formic acid – *tert*-butyl alcohol

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HIGHLIGHTS

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ABSTRACT

The rotational spectra of the parent and eight isotopologues of the 1:1 complex formic acid – *tert*-butyl alcohol (FA-TBA) have been measured by pulsed jet Fourier transform microwave spectroscopy. The spectra have been observed in the supersonic expansion of a mixture of FA and TBA in Helium, differently with respect to the mixtures of FA with primary and secondary alcohols, which undergo the esterification reaction upon supersonic expansion. In the complex, the two subunits are linked to each other by two different O-H...O hydrogen bonds (HB) in which FA and TBA are alternate their roles of bond acceptor and donor. Upon H → D substitution of the corresponding O-H...O HB, a small Ubbelohde effect is observed.

1. Introduction

Formic acid (FA) is the simplest carboxylic acid but its relatively high abundance in the troposphere [1] involves it in a rich series of reactions that can occur in the environment. [2–4] It has been observed that the dynamics of these reactions can be changed

when FA forms molecular adducts with different molecules. [2] Therefore the determination of the structures of the pre-reaction adducts is the key to understand and foresee the reactions trends.

Microwave spectroscopy combined with the supersonic expansion technique (FTMW) is one of the most suited tools to characterize molecules and molecular adducts in an environment free from matrix effects to obtain their energetics and structural features. Even small differences in the moments of inertia significantly change the resulting rotational spectrum and can differentiate between isomers, conformers, and isotopologues. In recent years this technique has been applied to disclose the noncovalent interaction features of clusters of FA (used as a molecular probe) with a number of different chemical compounds such as carbonyl derivatives, [5–16] nitrogen-containing molecules, [17–18] the simplest

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ether (dimethylether) [19] and other small molecules such as water, [20] difluoromethane [21] and carbon dioxide. [22] The variety of the established noncovalent interactions, ranging from O-H...O, O-H...N, N-H...O hydrogen bonds (HBs) to weaker HBs such as O-H...F, C-H...O HBs and finally to also O = C...O tetrel bond results in different structural and energetic features, with dissociation energies up to 60 kJ/mol.

Up to now, no microwave data are available on the interactions between alcohols and carboxylic acids. The reason of the failure of the detection of the pure rotational spectra of the adducts of carboxylic acids with alcohols in a supersonic expansion was discussed and explained in our previous work. [23] Primary and secondary alcohols react, indeed, to form the corresponding ester. This is confirmed in detail for the supersonic expansions of the mixtures of trifluoroacetic acid-methyl alcohol, [24] formic acid-cyclohexanol [25] and formic acid-isopropanol. [15] Ref. [23] outlines, however, that carboxylic acids can form the adduct with tertiary alcohols without any reactions in the absence of catalysts.

In this paper we report, indeed, the results of the investigation of the adduct of FA with a tertiary alcohol, *tert*-butyl alcohol, FA-TBA describing the hydrogen bond features linking the two subunits and providing chemical and energetic information on them.

2. Experimental section

The rotational spectra of FA-TBA, its five ^{13}C single substituted species (in natural abundance) and three monodeuterated isotopologues (HCOOD-TBA, DCOOH-TBA, HCOOH-TBA-OD) have been recorded using the COBRA-type [26] pulsed supersonic-jet Fourier-transform microwave (FTMW) spectrometer, [27] working in the 6–18.5 GHz frequency range and described elsewhere. [28]

Helium at stagnation pressure of 0.3 MPa was flown over separated reservoirs of TBA (Aldrich 98%) and FA (Aldrich 98%), and expanded through the solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry-Pérot-type cavity. The same procedure has been followed for the deuterated isotopologues whose respective monomers have been prepared either by direct H \rightarrow D exchange of FA or TBA with D_2O (Cambridge Isotope Laboratories), obtaining HCOOD or TBA-OD, or by using commercial sample (DCOOH, Aldrich, 95% wt).

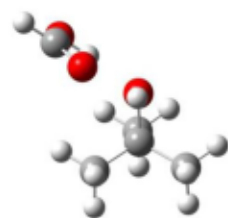
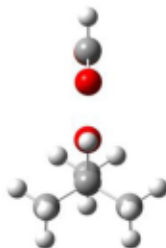
The rest frequency of each transition is calculated as the arithmetic average of the frequencies of the two Doppler components. The estimated accuracy of the frequency measurements is 3 kHz.

3. Theoretical calculations

According to the possible chemical behaviour of FA and TBA, the most stable clusters should involve O-H...O hydrogen bond type interactions in the complexes stabilization. In this respect, one stationary point isomer of FA-TBA, has been found at the MP2/6-311++G(d,p) [29] level, using the GAUSSIAN16 package. [30] All the rotational parameters (equilibrium rotational constants and electric dipole moment components) needed for the spectroscopic assignment are reported together with the corresponding dissociation energies (E_D), accounting for zero-point and BSSE corrections, [31] in Table 1. The shape of the isomer is shown at the top of the Table 1. Two O-H...O HBs link the two constituent molecules, leading to the formation of a six membered ring between the two subunits. This isomer belongs to the C_1 symmetry point group and has two equivalent (degenerate) forms since the FA subunits can interact in the same way on the two sides of the TBA subunit. In Table 1 are also reported the spectroscopic data and a sketch for the transition state, with a C_s symmetry, which connects those two equivalent forms, making the molecular adduct chiral. [32] The transition state is characterized by a negative frequency value (in

Table 1

MP2/6-311++G(d,p) equilibrium, zero point (ZPE) and BSSE corrected energies and spectroscopic parameters of the global minimum and of the transition state of FA-TBA.

| | C_1 | C_s |
|--------------------------------------|---|---|
| |  |  |
| $\Delta E/\text{kJ mol}^{-1}$ | 0 ^{a,b,c,d} | 2.85 Transition state |
| $E_{D(ZPE+BSSE)}/\text{kJ mol}^{-1}$ | 31.1 ^e | |
| A/MHz | 3300.7 | 3285.0 |
| B/MHz | 980.4 | 861.0 |
| C/MHz | 905.6 | 802.7 |
| μ_a/D | -1.76 | -2.08 |
| μ_b/D | 0.09 | 0.09 |
| μ_c/D | 1.02 | 0 |

^a Absolute energy: $E = -422.431986 E_h$.

^b Absolute energy + ZPE: $E = -422.258228 E_h$.

^c Absolute energy + BSSE: $E = -422.427197 E_h$.

^d Absolute energy + ZPE + BSSE: -422.253935 .

^e Dissociation energy, including zero-point energy (ZPE, harmonic approximation) and basis set superposition error (BSSE) corrections.

the harmonic approximation) and at this level of theory the height of the barrier for the interconversion of the two chiral forms is about 2.85 kJ/mol. For this kind of molecular complexes considering the energy barrier and the relative mass involved in the motion, we do not expect any observable tunnelling due to this internal motion. So the interactions between FA and TBA induces a permanent chirality in the adducts in the time scale of rotational spectroscopy.

3.1. Rotational spectrum

The theoretical stable isomer has a predicted high value of the μ_a -dipole moment component and for this reason, the first spectral search covered a frequency range where the $J: 5 \rightarrow 4$ μ_a -type R -band was expected to fall. Following this prediction, a set composed of intense transitions has been identified. The $5_{05} \rightarrow 4_{04}$ transition is shown in the right side of Fig. 1. Then many other μ_a -type R -band transitions (up to $J = 10$), μ_c -type lines and some much weaker μ_b -type have been measured for a total of 87 pure rotational transitions.

Later on, the rotational spectra of all five ^{13}C species (single substitution) in natural abundance have been assigned and measured. Finally, the spectra of the single deuterated HCOOD-TBA, DCOOH-TBA and HCOOH-TBA-OD isotopologues have been collected and assigned. Splittings due to the quadrupolar effects of the D atom ($I = 1$) have not been satisfactorily resolved. The respective transitions have been fitted by using the Pickett's SPFIT program, [33] within the F -representation of Watson's S reduction. [34] The results for the parent and ^{13}C species are reported in Table 2, while those of the mono-deuterated isotopologues are listed in Table 3. The obtained rotational constants are in good agreement with the theoretical values of isomer C_1 whose labeling of the ^{13}C and deuterated species is according to Fig. 2.

3.2. Structural information

The experimental rotational constants (3300.7, 974.3, 901.3 MHz, rounded at the first decimal digit) are very close to

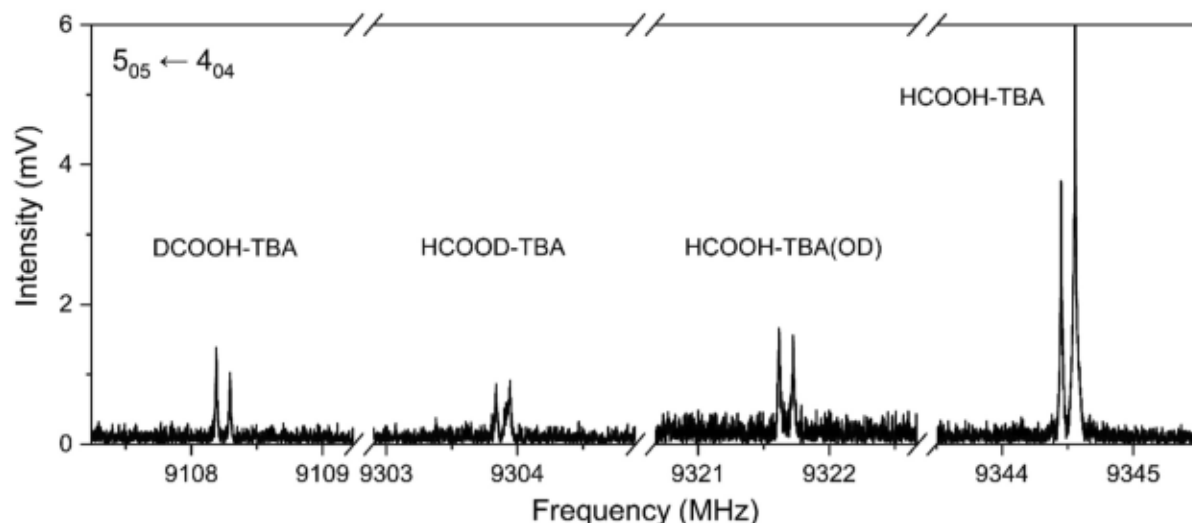


Fig. 1. The $5_{05} \leftarrow 4_{04}$ rotational transition for the most abundant (right) and the three deuterated species of the observed FA-TBA adduct.

Table 2

Experimental spectroscopic constants of the parent and ^{13}C species of FA-TBA (*S*-reduction, *F* representation).

| | Parent | $^{13}\text{C1}$ | $^{13}\text{C2}$ | $^{13}\text{C4}$ | $^{13}\text{C5}$ | $^{13}\text{C7}$ |
|--|---------------------------|-----------------------|------------------|------------------|------------------|------------------|
| <i>A</i> /MHz | 3300.7317(2) ^a | 3263.407(6) | 3300.943(2) | 3252.246(3) | 3267.594(8) | 3300.624(4) |
| <i>B</i> /MHz | 974.3274(1) | 965.6130(4) | 970.2808(1) | 967.9831(2) | 963.6966(5) | 960.6524(3) |
| <i>C</i> /MHz | 901.34322(9) | 891.1650(3) | 897.8793(1) | 899.3929(2) | 890.5315(4) | 889.6471(2) |
| <i>D_J</i> /kHz | 0.6396(6) | [0.6396] ^b | [0.6396] | [0.6396] | [0.6396] | [0.6396] |
| <i>D_{JK}</i> /kHz | 2.446(5) | [2.446] | [2.446] | [2.446] | [2.446] | [2.446] |
| <i>D_K</i> /kHz | -2.66(2) | [-2.66] | [-2.66] | [-2.66] | [-2.66] | [-2.66] |
| <i>d₁</i> /Hz | -52.3(5) | [-52.3] | [-52.3] | [-52.3] | [-52.3] | [-52.3] |
| <i>d₂</i> /Hz | 7.9(3) | [7.9] | [7.9] | [7.9] | [7.9] | [7.9] |
| <i>P_{aa}</i> /uÅ ² | 463.140 | 467.807 | 465.308 | 464.306 | 468.628 | 470.515 |
| <i>σ^r</i> /kHz | 2.8 | 4.6 | 2.0 | 3.0 | 6.1 | 3.4 |
| <i>N</i> ^d | 87 | 10 | 10 | 10 | 10 | 10 |

^a Standard errors in parenthesis are expressed in units of the last digit.

^b Parameters in the brackets fixed to the values of parent species.

^c Root-mean-square deviation of the fit.

^d Number of fitted transitions.

Table 3

Experimental spectroscopic constants of the three monodeuterated species of FA-TBA (*S*-reduction, *F* representation).

| | D9 | D10 | D11 |
|--|--------------------------|-------------|-------------|
| <i>A</i> /MHz | 3296.776(1) ^a | 3280.224(1) | 3257.260(1) |
| <i>B</i> /MHz | 948.3702(2) | 970.6993(2) | 972.9132(3) |
| <i>C</i> /MHz | 879.2999(3) | 897.0220(2) | 898.5602(3) |
| <i>D_J</i> /kHz | 0.599(2) | 0.627(2) | 0.599(2) |
| <i>D_{JK}</i> /kHz | 2.47(3) | 2.49(3) | 2.18(4) |
| <i>D_K</i> /kHz | -2.3(1) | -2.2(1) | -2.6(1) |
| <i>d₁</i> /Hz | -43(2) | -46(1) | -52(2) |
| <i>d₂</i> /Hz | [7.9] ^b | [7.9] | 7(1) |
| <i>P_{aa}</i> /uÅ ² | 477.174 | 464.981 | 463.363 |
| <i>σ^r</i> /kHz | 2.4 | 2.4 | 2.8 |
| <i>N</i> ^d | 27 | 28 | 28 |

^a Standard errors in parenthesis are expressed in units of the last digit.

^b Parameters in the brackets fixed to the values of parent species.

^c Root-mean-square deviation of the fit.

^d Number of fitted transitions.

the theoretical values (3300.7, 980.4, 905.6 MHz). Just increasing by 0.017 Å the O3-H10 bond length (see Fig. 2) from 1.7143 to 1.7313 Å in the *ab initio* geometry, we obtained an effective structure useful to reproduce within a few tenths of MHz the experimental rotational constants, and then a satisfactory reproduction

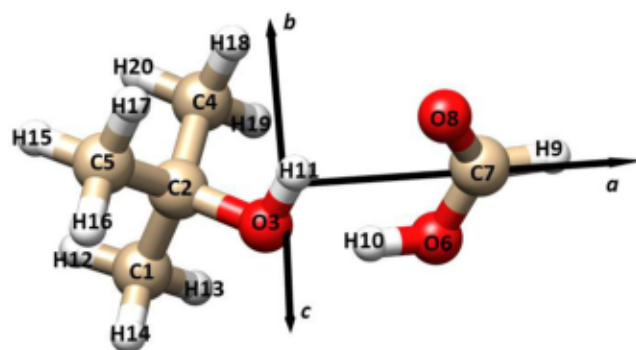


Fig. 2. Sketch of the observed isomer of FA-TBA showing atom numbering and principal axes of inertia.

of the planar moment of inertia of the observed isotopologues for isomer *C_f*.

The substitution coordinates (*r_s*) of five carbon atoms (C1, C3, C4, C5 and C7 of Fig. 1) and of three hydrogen atoms (H9, H10 and H11 of Fig. 1) have been calculated according to the Kraitchman's equations [35] thanks to the availability of the nine isotopologue sets of rotational constants.

Table 4

r_s and r_e (MP2/6-311++G(d,p)) coordinates of the substituted atoms in the principal axis system of the parent species of FA-TBA.

| | $a/\text{\AA}$ $ r_s $ | r_e | $b/\text{\AA}$ $ r_s $ | r_e | $c/\text{\AA}$ $ r_s $ | r_e |
|-----|---------------------------|---------|---------------------------|---------|---------------------------|---------|
| C1 | 2.1605(7) ^a | -2.0836 | 1.329(1) | 1.3718 | 0.12(1) | -0.0704 |
| C2 | 1.476(1) | -1.4728 | 0.07 ⁱ (2) | -0.0177 | 0.07 ⁱ (2) | 0.0356 |
| C4 | 1.080(1) | -1.0875 | 0.217(7) | -0.3435 | 1.501(1) | 1.4770 |
| C5 | 2.3436(6) | -2.4097 | 1.157(1) | -1.0786 | 0.495(3) | -0.5333 |
| C7 | 2.7225(6) | 2.7168 | 0.06 ⁱ (2) | -0.0044 | 0.09(2) | 0.1017 |
| H9 | 3.7493(4) | 3.7455 | 0.15(1) | 0.1892 | 0.410(4) | 0.4309 |
| H10 | 1.357(1) | 1.1329 | 0.929(2) | 0.8993 | 0.316(5) | -0.3442 |
| H11 | 0.472(3) | 0.1743 | 1.224(1) | -0.8222 | 0.742(2) | -0.7054 |

^a Errors in parenthesis are expressed in units of the last digit.

Table 5

Theoretical (r_e , MP2/6-311++G(d,p)) and r_s geometries (the imaginary value has been set to zero) of the carbon mainframe of FA-TBA.

| Bond lengths/ \AA | Valence angles/ $^\circ$ r_s/r_e | Dihedral angles/ $^\circ$ r_s/r_e | r_s/r_e |
|----------------------------|---------------------------------------|--|----------------|
| C2C1 | 1.50(2)/1.521 | C1C2C7 | 117.3(7)/113.6 |
| C2C4 | 1.57(2)/1.527 | C4C2C7 | 74.1(2)/74.5 |
| C2C5 | 1.53(2)/1.525 | C5C2C7 | 125.1(8)/128.5 |
| C2C7 | 4.200(1)/4.190 | | |

The obtained data are summarized in Table 4, and there compared with those resulting from the MP2/6-311++G(d,p) calculations.

In Table 5, we compare the r_s and r_e structural parameters of the mainframe of the five carbon atoms, with C2 of Fig. 2 being at the center of this mainframe.

The substitution coordinates of atoms close to the center of mass should be considered with caution, [36] as well as those of hydrogen atoms involved in hydrogen bond, because of the Ubbelohde effect.

The mentioned Ubbelohde effect was first discussed by Ubbelohde and Gallagher, [37] who observed in crystal structure that the H \rightarrow D isotopic substitution of the hydrogen atom involved in the non-covalent interaction increases the length of the hydrogen bond itself. Further studies in gas phase have shown that such effect characterizes also the double hydrogen bond of the dimers of carboxylic acids (see, for example, Ref. [9]), since it is mainly related to the double minimum potential associated with the concerted proton transfer that can take place in these bimolecules. Vice versa, in molecular adducts which are made of two subunits held together by only a single hydrogen bond (such as O-H...O, O-H...N, etc.), a shrinkage of the O...O or O...N distance is observed. In this case the finding is called inverse Ubbelohde effect, [38] as discussed in refs. [13–17,22].

Surprisingly in the present case we note an increase of the length of the hydrogen bonds O3-H11...O8 and O3-H10...O6 upon H \rightarrow D isotopic substitution of either H10 or H11. These elongations are proved by increases of the planar moments of inertia P_{aa} of 0.224 and 1.841 uÅ² in going from the parent to the TBA-OD and HCOOD species, respectively, while the “rigid” model would imply an increase of 0.027 and 1.307 uÅ². Increase of ~ 1 mÅ and of ~ 3 mÅ for the H11...O8 and H10...O6 bond lengths, respectively, account for the observed unexpected changes of the P_{aa} values. There are three main components which generates the Ubbelohde effect. As mentioned before in the text, the first a) is due to the double well potential energy surface in strongly hydrogen bond systems which play the central role for dimer of carboxylic acids. In this molecular system there is a six atoms ring containing two hydrogen bonds which is, indeed, almost planar. However, the double hydrogen exchange does not connect two equivalent minima. Anyway, two other effect are involved in the “classical” Ubbelohde effect: b) the increase of anharmonicity

stretching vibration moving from -O-H to -O-D; and c) the contribution to the non-covalent bond of the -O-H bending. Although these contributions can be difficult to quantify individually and their complete theoretical treatment is beyond the scope of this work, we can affirm that their contribution is manifested in the observed “classical” Ubbelohde effect.

4. Conclusions

In previous experimental observations it was realized that, within the experimental conditions outlining FTMW investigations, FA reacts with primary and secondary alcohols to form the ester. Here we show that in the same kind of experiment, when FA is combined with the tertiary alcohol TBA, the molecular adduct is observed, but not the ester.

The rotational spectra of nine isotopologues of FA-TBA have been characterized by FTMW spectroscopy and prove that the two subunits are linked together by two classical O-H...O hydrogen bonds, inserted in a six-membered ring.

Elongations of about 1 and 3 mÅ upon single H \rightarrow D substitution of the hydrogen atoms contained in the two O-H...O hydrogen bonds denote a “classical” Ubbelohde effect.

Associated Content

Supporting Information. 1) Completion of Reference 30. 2) Tables of the transition frequencies. 3) MP2/6-311++G(d,p) coordinates of the atoms of FA-TBA.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.saa.2021.119621>.

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