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COMMENTS

Comment on “Computational Investigation of $SO_3-NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) Interactions”

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The weakly bound complexes of SO_3 with simple inorganic and organic molecules are intensively investigated as exemplary cases of noncovalent intermolecular interactions and as a means to better understand fundamental atmospheric processes.[1−6] In particular, in a very recent study,[7] Solimannejad and Boutalib have theoretically investigated the interaction of SO_3 with $NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl). Assuming that all these ligands behave as nitrogen donors, they computed the MP2(full)/6-31G(d) geometries of the $SO_3-NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) complexes and evaluated their stability in terms of the energy, enthalpy, and free energy changes of the association

$$SO_3 + NH_{3-n}X_n \rightarrow SO_3-NH_{3-n}X_n \qquad (1)$$

At the G2(MP2) level of theory,[8] the ΔE(0 K) of (1) resulted as −17.5 kcal mol^{-1} for SO_3-NH_3 and reduced to −14.2, −11.3, and −9.8 kcal mol^{-1} for SO_3-NH_2Cl, SO_3-NHCl_2, and SO_3-NCl_3, respectively. For SO_3-NH_2F, SO_3-NHF_2, and SO_3-NF_3, the reductions with respect to SO_3-NH_3 were invariably larger and the interaction energies were computed as −11.6, −6.1, and −3.0 kcal mol^{-1}, respectively. The variations in the bond lengths and in the bond angles observed passing from SO_3-NH_3 to $SO_3-NH_{3-n}X_n$ ($n = 1-3$; X = F, Cl) were discussed in terms of natural bond orbital analysis, and a good linear relationship was also established between the complexation energies and the proton affinities of the Lewis bases $NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl). Thus, Solimannejad and Boutalib[7] conclude that the successive fluorine and chlorine substitution on NH_3 decreases the basicity of the N atom of the ligand and results in a regular decrease of the stability of the nitrogen-coordinated $SO_3-NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) complexes. However, in our opinion, at least for the fluorinated species, any complete description of the structure and stability of the $SO_3-NH_{3-n}F_n$ ($n = 1-3$) adducts cannot leave out of consideration the numerous experimental and theoretical studies[9−15] which indicate that, when interacting with ionic[9−14] as well as neutral[15] electrophiles, nitrogen trifluoride, NF_3, may behave as a bifunctional Lewis base, able to form N- and F-coordinated isomers of comparable stability. In addition, the predicted accuracy of G2(MP2) thermochemical estimates, ca. 3 kcal mol^{-1},[8] does not allow any definitive conclusion on a bound SO_3-NF_3 adduct, whose stabilization energy is computed as just 3 kcal mol^{-1}. Therefore, we decided to use the G3 theory, whose predicted accuracy is ca. 2 kcal mol^{-1},[16] to investigate the structure and stability of the N-coordinated isomer **1a** and of the F-coordinated isomer **1b** of the $SO_3-(NF_3)$ complex. The results of our calculations, performed with the Gaussian 98 set of programs,[17] are shown in Figure 1. Similarly to **1a**, isomer **1b** is a true minimum on the MP2(full)/6-31G(d) potential energy surface and results a weakly bound adduct between SO_3 and NF_3. The S−F distance is as long as 2.87 Å, and the geometries of the two moieties are essentially unperturbed with respect to the uncoordinated molecules. Consistently, at the G3 level of theory, the complexation energy at 0 K of **1b** results as low as −3.1 kcal mol^{-1} (the G2(MP2) estimate is −2.2 kcal mol^{-1}). This value is, however, lower than that for **1a** by less than 1 kcal mol^{-1}, and both complexation energies of **1a** and **1b** are larger than the G3 uncertainty of ca. 2 kcal mol^{-1}. Thus, our calculations remove the theoretical ambiguity on the actual existence of a bound $SO_3-(NF_3)$ complex and suggest also that the ligation of NF_3 to SO_3 may occur not only by nitrogen, as suggested by Solimannejad and Boutalib,[7] but also by fluorine.

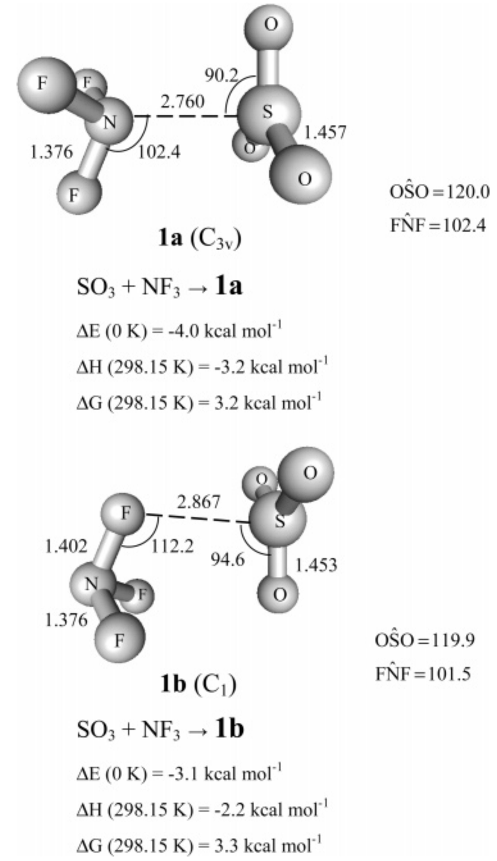

Figure 1. MP2(full)/6-31G(d) selected optimized bond lengths (Å) and bond angles (deg), and G3 thermodynamics of complexation of the $SO_3-(NF_3)$ isomers **1a** and **1b**.

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Concerning the relative stability of the $SO_3{-}NH_{3-n}F_n$ ($n = 1{-}3$) adducts, it is difficult, in our opinion, to get a definitive conclusion on the order of the quite close complexation energies of the weakly bound $SO_3{-}NHF_2$ and $SO_3{-}NF_3$ adducts.

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