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A Remarkable, Stable Radical–Molecule Complex: $HO_2 \cdot CF_3C(O)OH$

Joseph S. Francisco

The hydrogen bond is of considerable interest in understanding the structure and energetics in a wide range of chemical systems.[1–3] Many studies have examined hydrogen bonding in neutral molecule–molecule and ion–molecule complexes,[4] but few have focused on radical–molecule complexes. A vigorous research effort is just beginning to examine fundamental questions of hydrogen bonding in open-shell complexes. Molecular complexes are generally weakly bound[5, 6] and hence relatively short-lived. Such complexes are reported to play key roles in the Earth's atmosphere.[7] Strongly bound complexes of atmospheric species suggest long atmospheric lifetimes, and this leads to the possibility of their being transported to remote regions of the atmosphere, where their concentration profiles are not expected to be large. The atmospheric oxidation of alternative fluoro- and chlorofluorocarbons, such as HFC-134a, HCFC-123, and HCFC-124, is a major atmospheric source of trifluoroacetic acid (TFA).[8, 9] Because of the increased use and production of alternative chlorofluorocarbons, TFA concentrations are projected to increase.[10] Trifluoroacetic acid is chemically and biologically stable and highly resistant to photochemical breakdown. To date, little evidence is available for the degradation of TFA; consequently, little is known about the consequences of trifluoroacetic acid for atmospheric chemistry. Here we report on density functional calculations that suggest the existence of a complex between trifluoroacetic acid and $HO_2^{\bullet}$ radicals. The structural and energetic data of the complex suggest novel bonding and stability that have important ramifications for the atmospheric role of trifluoroacetic acid.

Unrestricted density functional calculations with Becke's three parameters and Lee–Yang–Parr functionals (UB3LYP)[11, 12] with the 6-311++G(3df,3pd) basis set were carried out. The fully optimized geometries with minimum energies were confirmed to be stable minima by vibrational frequency analysis.[13] Only the global minimum energy structure is reported in this study. The structure of $HO_2 \cdot CF_3C(O)OH$ (Figure 1) is characterized by two hydrogen bonds, labeled R1 and R2. The hydrogen bond between the hydrogen atom of the hydroperoxyl radical and the carbonyl oxygen atom of the trifluoroacetic acid has a length of 1.685 Å, as does that between the hydroxyl hydrogen atom of trifluoroacetic acid and the terminal oxygen atom of the hydroperoxyl radical. These bonds are both significantly shorter than the typical hydrogen-bond lengths in the water dimer (ca. 1.95 Å) and in the well-studied formic acid/H_2O complex (1.786 Å). Unlike weakly bound complexes, in which the structures of the components are virtually unaffected by hydrogen bonding, there is a significant degree of structural perturbation of the geometry of the two components as a result of the bonding in the $HO_2 \cdot CF_3C(O)OH$ complex. The C–O′ bond in trifluoroacetic acid is shortened by 0.032 Å (i.e., 2.4 %), and the O–H bond is lengthened by 0.037 Å (i.e., 3.8 %). The O–H bond length in the $HO_2^{\bullet}$ radical in the complex is lengthened by 0.029 Å (i.e., 3.0 %) relative to isolated $HO_2^{\bullet}$. These structural changes indicate strong interactions in the $HO_2 - CF_3C(O)OH$ complex.

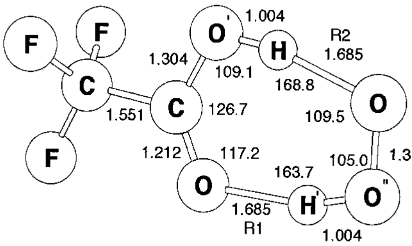

Figure 1. Structure and geometry of $HO_2 \cdot CF_3C(O)OH$.

The bonding energies at various levels of theory are presented in Table 1. At the highest level of theory, the binding energy D_o and well depth D_e of $HO_2 \cdot CF_3C(O)OH$ are 15.1 and 17.1 kcal mol^{-1}, respectively. Considering that the water dimer[14–16] has a well depth of about 4.8 kcal mol^{-1}, this is tremendous. Typically, hydrogen bonds have energies of 2–7 kcal mol^{-1} and are thought to involve essentially linear arrangements of donor and proton acceptors.[1, 16, 17] In this case, each component acts as a hydrogen donor and acceptor,

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Table 1. Calculated binding energies for $HO_2 \cdot CF_3C(O)OH$.

Level of theory	D_e	D_o
B3LYP/6-31G(d)	21.3	19.3
B3LYP/6-311++G(d,p)	17.1	15.1
B3LYP/6-311++G(2d,2p)	16.8	14.8
B3LYP/6-311++G(2df,2p)	16.8	14.8
B3LYP/6-311++G(3df,3pd)	17.1	15.1

and a cyclic arrangement is created by the formation of two hydrogen bonds. This also occurs in the dimers of formic and acetic acids,[2] for which binding energies of 12–15 kcal mol^{-1} were measured. Note that these interactions are between two closed-shell molecules, while the interaction between $HO_2^{\bullet}$ and $CF_3C(O)OH$ is between open- and closed-shell molecules.

The chlorine oxide dimer ClOOCl plays important roles in the chemistry of polar ozone depletion. This species is bound by about 17.0 ± 2 kcal mol^{-1},[18, 19] and is held together by weak covalent bonding. The dimer of NO_2 (N_2O_4) is another important atmospheric species that is held together by weak covalent bonding (ca. 13.6 kcal mol^{-1}).[19] The strong hydrogen bonding in the $HO_2 \cdot CF_3C(O)OH$ complex is on the order of magnitude of weak covalent bonds.

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