Aldehyde Hydration in Aqueous Solution: Estimating Activation Free Energy for Perfluoroaldehyde

Osamu Setokuchi

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan
Corresponding author: o.setokuchi@aist.go.jp

T U E S D A Y

Aldehydes, formed in oxidation of VOCs, are removed mainly by photolysis and reaction with OH radicals in the atmosphere. The reaction with water molecules[1] also can play an important role in eliminating some aldehydes in gas and the condensed phase. Aldehyde hydration in media such as cloud droplets and aqueous aerosols is an important process in understanding the source of carboxylic acid in the atmosphere, since the reaction product diols can be converted into acid by reacting with OH radicals.[2] Much attention has been paid to hydration of reactive α-dicarbonyls and perfluoroaldehydes (PFAs) as the source of dicarboxylic acids found in aerosols[3] and perfluorocarboxylic acid (PFCAs) detected in rain.[4] PFAs are degradation products of fluorotelomer compounds. The experimental reaction rates for diol formation of perfluoroaldehyde, however, have not been measured in aqueous solution.

In this study, I calculated the activation Gibbs free energy ($\Delta G^{\neq}$) of hydration for some aldehydes RCHO (R=H, CH_3, CCl_3, CF_3 and C_2F_5), using a water-cluster and polarizable continuum hybrid model. I compared calculated $\Delta G^{\neq}$s with available experimental values to estimate the rate constant for diol formation of CF_3CHO and C_2F_5CHO in aqueous solution. The geometry was optimized at the double hybrid DFT level with empirical dispersion correction. Though the water cluster models are based on the cyclic proton transfer reaction mechanism containing three water molecules proposed by Bell et al.,[5] they involve some additional micro-solvated water molecules. The increased number of water molecules leads to formation of intermediates (ion-pair complex) via a stepwise mechanism.[6] When the cluster models with seven water molecules are employed, two cluster models are produced, one with a stepwise mechanism (model A) and one with a concerted mechanism (model B), depending on the orientation of water molecules in the hydrogen-bonding network. The electron-withdrawing group favors the formation of an ion-pair complex more than the electron-donating group in model A. In model A, the bottleneck that determines the hydration rate is the transition state connecting the encounter complex and the ion-pair complex. Both Models A and B predict one to two magnitude larger rate constants for CF_3CHO and C_2F_5CHO than for CCl_3CHO.

Acknowledgements

References
(1) Vaida, V. *J. Chem. Phys.* **2011**, 135, 020901.
(2) Andersen, M. P. Sulbaek; Toft, A.; Nielsen, O. J.; Hurley, M. D.; Wallington, T. J.; Chishima, H.; Tonokura, K.; Mabury, S. A.; Martin, J. W.; Ellis, D. A. *J. Phys. Chem. A* **2006**, 110, 9854-9860. (3) Lim, Y.B.; Tan, Y.; Perri, M.J.; Seitzinger, S.P.; Turpin, B.J. *Atmos. Chem. Phys.* **2010**, 10,10521-10539. (4) Scott, B.F.; Spencer, C.; Mabury, S.A.; Muir, D.C.G. *Environ. Sci. Technol.* **2006**, 40**,** 7167-7174. (5) Bell, R.P.; Millington, J.P.; Pink, J.M. *Proc. R. Soc. London, Ser. A* **1968**, 303, 1. (6) Wang, B.; Cao Z. *Angew. Chem. Int. Ed.* **2011**, 50, 3266-3270.