

Catalytic effect of water on the $\text{CH}_3\text{OH} + \text{OH}$ reaction under quasi-real atmospheric conditions

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The effect of water in the atmospheric chemistry is of great importance. Recent, experimental and theoretical works have suggested that at low temperature one water molecule is enough to catalyze reactions of the OH radical with several Volatile Organic Compounds (VOCs), through the formation a H-bonded complex between the OH, the VOC and the H_2O molecule.^{1,2} However, this effect has not been evidenced at room temperature, yet, due to the very low concentration of these complexes under atmospheric conditions.³

In this work, the rate constant for the $\text{OH} + \text{CH}_3\text{OH}$ reaction, has been determined by means of a relative method, under quasi-real atmospheric conditions (295 K and 1 atm of air as buffer gas), at variable concentration of water (relative humidity: % H_R).

The dependence of the rate constant of the title reaction on the % H_R , determined using n-pentane as reference compound, is shown in the Figure. A quadratic dependence can be observed, indicating that two water molecules are necessary to catalyze the reaction under atmospheric conditions. It is worth noting that the extrapolated rate constant at 0 % H_R is in very good agreement with the literature recommended value determined under dry conditions.⁴ Theoretical calculations at several level have been performed that allow rationalizing the experimental results considering the formation of H-bonded complexes that undergo to product without any energy barrier. The absence of the catalytic effect with only one water molecule can also be explained by the calculations.

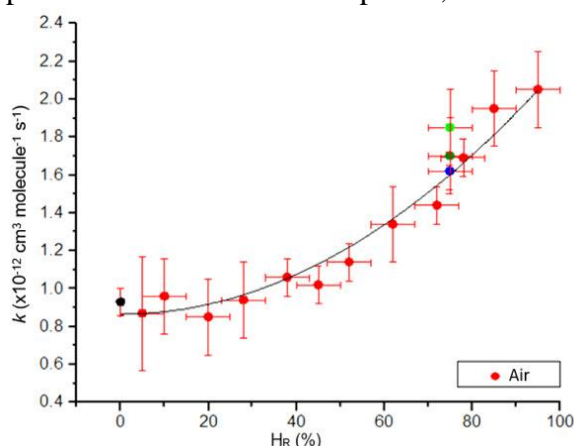


Figure: Dependence of the rate constant for the reaction title on the relative humidity (%RH)

References

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