HOW INTERMOLECULAR INTERACTIONS EFFECT ESTERIFICATION REACTIONS? A MICROWAVE STUDY OF THE GAS-PHASE COMPLEXES OF FORMIC ACID WITH TWO METHANOL DERIVATIVES AND THEIR ESTERIFICATION PRODUCTS.

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Esterification is a reaction of great interest and importance in organic and biological chemistry, where typically an alcohol and a carboxylic acid react and form an ester as the product. Previously, by exploring gaseous mixtures of formic acid (FA) with various alcohols using rotational spectroscopy, it has been found that primary and secondary alcohols tend to readily form an ester by reacting with FA, whereas the tertiary alcohol-FA adduct remains unreacted.[a] Herein, we present the microwave spectroscopic study of FA with two primary alcohols, 3-methyl-3-oxetanemethanol (MOM) and cyclobutanemethanol (CBM), in the gas phase. The spectra in the frequency span of 18-26 GHz were collected on our newly built segmented chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer.[b] Both of the esterification products have been unambiguously assigned with multiple structural conformations. Interestingly, their pre-reaction complexes, MOM-FA and CBM-FA, are observed in the spectra as well. Different from CBM-FA, whose ester product is more pronounced than the adduct in the spectrum, the reaction of MOM with FA seems to be more slowly. This could be attributed to the presence of relatively stronger intermolecular interactions in MOM-FA, compared to CBM-FA. Quantum-chemical calculations were performed to have a deeper insight into their reactivity.

[a] L. Evangelisti, L. Spada, W. Li, F. Vazart, V. Barone, and W. Caminati, Angew. Chem. Int. Ed. Engl. **56**, 3872-3875 (2017).
[b] M. Fatima, C. Pérez, B. E. Arenas, M. Schnell, and A. L. Steber, Phys. Chem. Chem. Phys. **22**, 17042-17051 (2020).