

The reaction of diethyl ether with OH radicals: rate coefficient, kinetic isotope effect, and mechanism

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Ethers gain increasing importance as prospective fuel additives/substitutes.¹ Accordingly, their combustion as well as their atmospheric degradation are of considerable scientific interest. In both reaction systems, the ether + OH reaction plays a key role. Moreover, it is of fundamental kinetic interest as a prominent example for pre-reactive complex formation.^{2,3}

In our contribution we report on a combined experimental and theoretical study on the kinetics and mechanism of the reaction of diethyl ether (DEE) with OH radicals and compare it with the analogous reaction of dimethyl ether (DME).^{2,3} To gain additional kinetic information, we also studied the isotope effect, using the perdeuterated ethers. Our experiments were performed in the temperature range 290–650 K at pressures between 6 and 22 bar. The OH radicals were produced by laser flash-photolysis of HNO₃ and detected time-resolved by laser-induced fluorescence. Rate coefficients were determined under pseudo-first order conditions with respect to OH.

The experimentally obtained rate coefficients for OH + DEE exhibit a different temperature dependence compared to those of the previously studied OH + DME reaction.^{2,3} Whereas the rate coefficient in the latter case increases with temperature, a slight decrease was observed for the former reaction. Furthermore, the isotope effects and their temperature dependences differ. For both reactions quantum-chemical calculations predict a complex-forming mechanism via reversible OH-ether adduct formation and subsequent intramolecular hydrogen abstraction. Statistical rate theory calculations show that the differences in the rate coefficients and the isotope effects can be consistently explained by different barrier heights of the intramolecular abstraction step and different bond-dissociation energies for back dissociation of the corresponding adduct. In this way, the two reactions turn out to be a nice illustration of how small variations in the potential energy surface can lead to qualitatively different kinetic behavior.

From a comparison of the experimental results with predictions from canonical transition state theory including corrections for tunneling and hindered internal rotations, we could also confirm that the steady-state approximation for the collisionally stabilized OH-ether adduct is an appropriate assumption under the conditions of our experiments

References

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