Impact of Kinetic Temperatures in Microwave Heating

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Microwave heating in polar solvents provides for an increased reaction rate constant and an improved yield compared to the conventional heating by thermal conduction,[1] which provides a thermal equilibrium with a homogeneous temperature: molecules, atoms and electrons have the same temperature.

This presentation pursues a theory for the microwave effect herein. Under the microwave irradiation, the reaction system is in a non-thermal equilibrium with heterogeneous kinetic temperatures, each of which correlates to an average kinetic energy of particles.

In the prominent Arrhenius equation (1) shown below, where k is a reaction rate constant; A is a frequency factor; E is the activation energy; R is the universal gas constant; and T should be an electron temperature, which is a kinetic temperature of electrons, instead of absolute temperatures defined in the thermal-equilibrium thermodynamics. Any chemical reaction involves the cleavage and formation of chemical bonds, which correspond to the changes in the spatial distribution of the electron probability density, and the electrons in the reactants play the dominant role during the chemical reaction. The external electric field by microwave gives drastically increased electron temperatures in any ion, which includes carbocations, carbanions and electrolytes, compared to kinetic temperatures of the atoms in the ion since the external electric field at the positions of the atoms are shielded by the electrons. With regard to the frequency factor A, the electromagnetic energy of microwave increases rotations of the polar solvent, which is equivalent to an increased kinetic temperature of the polar solvent in rotation in contrast to the kinetic temperature of the polar solvent in translation, so as to give the increased frequency factor.

$$k = Aexp\left(-\frac{E}{RT}\right) \qquad (1)$$

1) Á. Díaz-Ortiz, P. Prieto, A. De La Hoz. *Chem. Rec.* **2019**, *19(1)*, 85.