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Microwave-assisted nitric acid digestion of organic matrices

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Activation energy values, calculated for microwave-assisted oxidation of organic substances from direct pressure and temperature measurements, have confirmed the identity of the oxidation decomposition mechanisms operating under thermal and microwave heating.

The effects taking place when using microwave radiation for the acceleration of chemical and physical processes are so significant that chemists who have applied these microwave systems for the dissolution of samples in the routine analysis of various objects[1–4] speak of a 'microwave revolution' in sample preparation.[5] The theoretical aspects of microwave-assisted decomposition have not been considered since the paper of Kingston and Jassie,[6] in which thermodynamic equations were used in the calculation of heating parameters based on direct temperature measurements.

The first steps in the detailed investigation of microwave-assisted oxidation of organic matrices with nitric acid were made in several papers,[7–11] in which the similarity of the main oxidation products under microwave and thermal heating was demonstrated. The similarity of the oxidation mechanisms can therefore be assumed. However, the oxidation kinetics are quite different, and the oxidation time at the same temperature is much longer for conventional heating than for microwave heating.[11] The possibility of comparing the qualitative characteristics of oxidation, *e.g.* activation energy (E_a), seems to be important for an understanding of microwave effects. An attempt to solve this complicated experimental task has only been made once, by Pratt.[12]

The work presented here is devoted to the development of a method for the estimation of E_a for the microwave-assisted oxidation of organic substances, directly from actual measurements of temperature and pressure in the system.

The rate of the chemical process depends on temperature according to the Arrhenius equation:

$$k = A\exp(-E_a/RT)$$

where k is the rate constant, A is the frequency factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature.

For the evaluation of E_a for different processes a method using continuous temperature rise was proposed[13,14] (the so-called 'dynamic method'). The method is based on the fact that for a first-order reaction in the absence of side processes, the rate constant is proportional to the quantity of substance formed; under these conditions the use of a logarithmic relationship between a parameter which is proportional to the quantity of substance formed and reciprocal temperature is appropriate.

Table 1 E_a values of organic substances, determined from experiments under microwave heating.

Class of organic substances	Individual substances	Activation energy/ kJ mol^{-1}
Hydrocarbons	Saccharose	73.3
	Galactose	73.5
Amino acids	Lysine	24.0
	Phenylalanine	50.0 (50.0[a])
	Tryptophan	32.0 (29.8[a])

[a]Data obtained by Pratt.[12]

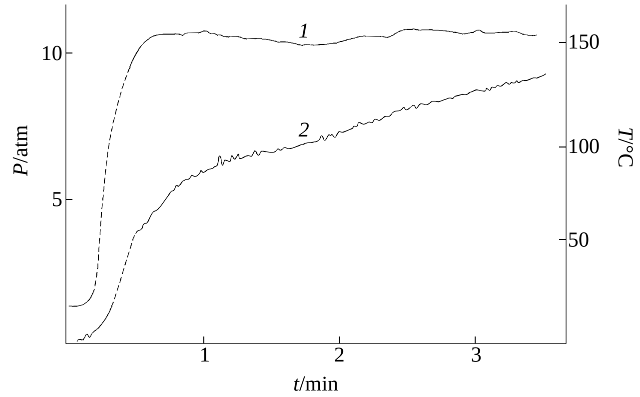

Figure 1 Temperature (*1*) and pressure (*2*) in a closed vessel *versus* time during the microwave-assisted oxidation of tryptophan with nitric acid.

Modern, commercially available microwave digestion systems, supplied with a sensor for direct temperature measurements and fitted with a pressure controller, seem to be ideal for carrying out such experiments. These can therefore be used in the investigation of processes for which a pressure change in the system takes place, in part, as a result of the formation of gaseous products.†

The basis for the use of a dynamic method in the evaluation of E_a when studying the oxidation of organic substances lies in the pressure change in a closed vessel. In the initial stage of the reaction this change is proportional to the rate of formation of oxidation products (mainly CO_2, because NO_2 is soluble at high pressures), *i.e.* to the decomposition rate. Thus, simultaneous measurement of the pressure in a closed vessel and the temperature of the reaction mixture (condensed phase) makes it possible to calculate the activation energy directly from the experimental data.‡ The absence of any effect due to substance quantity, as well as the shape of the curve obtained, confirm the first-order rate constant. It has also been shown that the side effects connected with the partial solubility of gaseous reaction products and with vaporisation of water are negligible.

To verify this possibility, we calculated E_a for individual compounds (amino acids, saccharose), chosen according to the composition of the most important natural substances

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† *Equipment.* Experiments were carried out using a laboratory microwave digestion system MDS-2000 (2450 MHz, 600 W) (CEM Corp., USA) in closed vessels LDV (pressure control up to 15 atm) and HDV (40 atm). The temperature of the reaction mixture was measured using a fibre optic probe in the range 20–200 °C.

Investigation technique. For oxidation, 0.1–0.4 g of sample was placed in a vessel of volume 100 ml, and 3–4 ml of concentrated HNO_3 (56%) and 0–1 ml of H_2O were added. After connection of the pressure and temperature sensors to the vessel, the parameters were measured every 5–15 s during 10–20 min. To estimate E_a, experimental data on pressures at elevated temperatures in the form of a logarithmic relationship between pressure and reciprocal temperature were used. E_a was calculated from the slope of a straight line and obtained using a least-squares method.

‡ This approach can also be more strongly argued.

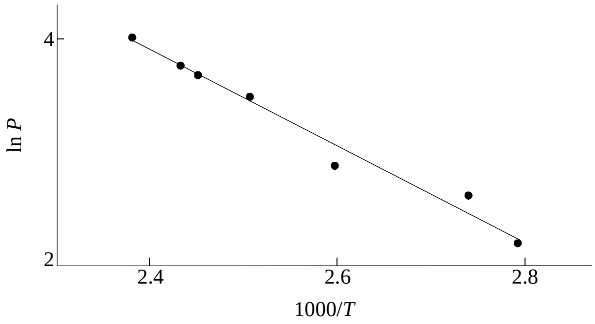

Figure 2 Arrhenius plot for the microwave-assisted oxidation of tryptophan with nitric acid.

(proteins and hydrocarbons). The values obtained lie within a conventional range for E_a, characteristic of such reactions (40–120 kJ mol^{-1}), and these correlate with the strength of the chemical bonds in the compounds. The most important feature is the good coincidence of the E_a values obtained in our work, using the dynamic method for phenylalanine and tryptophan, with the results obtained by Pratt[12] using the electrochemical detection of amino acid decomposition products at various temperatures (static method). Figure 1 shows the temperature and pressure changes in the system with time during the oxidation of tryptophan with nitric acid; in Figure 2 an Arrhenius plot is presented. Data calculated for several compounds are given in Table 1.

The data obtained allow us to conclude that: i, fast and simple determination of E_a from microwave heating of reaction mixtures directly from current measurements is possible; ii, the E_a values coincide for oxidation under both traditional and microwave heating.

According to the Arrhenius equation, the rate constant can increase in two cases: due to decreasing activation energy, *i.e.* if the mechanism is changed; or due to increasing factor *A*, which depends on the frequency and efficiency of collisions. The second reason, closely connected with the mechanism of microwave heating, can be assumed to be the major factor causing a significant acceleration of chemical processes in a microwave field.

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