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Fast determination of reaction kinetic parameters with the use of microwave heating. Kinetics of decomposition of organic substances with nitric acid

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A mathematical model for the kinetics of a chemical reaction under microwave irradiation in a close volume in the simplest approximation of the uniform temperature and pressure distribution in a system was proposed. The previously proposed dynamic method for determination of the activation energy of oxidation of organic substances with nitric acid was substantiated. According to this method, the activation energy is determined from the experimental exponential plot for the pressure in the nonisothermic system *vs.* inverse temperature of the reaction mixture.

Key words: microwave heating, kinetics, mathematical model, activation energy, oxidation of organic substances, nitric acid, oxalic acid, phenylalanine, trypthophan.

An increase in the temperature of reaction mixtures seems to be the most popular way for acceleration of chemical reactions. One of the methods for heating (alternative to the standard thermal method) is the absorption of electromagnetic microwave energy by a substance. The distinctive features of heating by microwave (MW) irradiation is its dependence on the dielectric characteristics of components of a reaction mixture and the high time and volume gradients created in the system at the microlevel and providing fast and uniform heating of a solution.[1,2] Effects related to the orienting action of the electromagnetic field can also appear.[3]

We have previously[4] proposed an approach to study microwave-assisted chemical processes. The approach includes a comparison of reaction rates under conditions of thermal and microwave heating, analysis of the composition and yield of formed compounds, and calculation of the activation energy. The use of this approach for studying hydrolysis of organic and inorganic compounds, complexation in solutions and heterogeneous systems, and oxidation of organic compounds with acids showed that the MW irradiation does not change the route of reactions, although considerably accelerates them and makes it possible to control purposefully the yield of reaction products. In the framework of this approach, we proposed[5] the dynamic method to determine the activation energy from current parameters of the nonisothermic process using the Arrhenius equation. An advantage of the dynamic method is that its use requires no particular isothermic kinetic experiments at different temperatures and the experiment itself takes much shorter time. The method of determination of the activation energy at continuously changing temperature was applied to the study of the kinetics of different processes, including those in enzymatic catalysis,[6] and to the mechanism of atomization in electrothermal atomic absorption spectrometry.[7] We used[5,8] the method based on direct measurements of the pressure and temperature in a reaction system to study oxidation of organic substances with nitric acid. The oxidation processes were demonstrated to be identical under thermal and microwave heating conditions. It was shown that the conditions and results of oxidation of organic substances with mineral acids can be simulated and predicted. However, an applicability of this method was substantiated only at a qualitative level.[5,8] This method should be justified more rigidly for a correct calculation of quantitative characteristics using the current parameters of the process. An extension of possibilities of microwave systems transforms them from heating devices into a tool for quantitative studies of chemical reactions.

In this work, we considered in detail and substantiated the physical model of the process under study and developed a mathematical apparatus for calculation of the activation energy.

Experimental

Reagents and materials. Oxalic acid and amino acids phenylalanine and tryptophan (Reanal, Hungary) were used as model compounds for studying oxidation under MW irradiation. Con-

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centrated HNO_3 (56%) and its mixtures with water served as oxidizing agents.

Apparatus. Experiments were carried out in an MDS-2000 microwave digestion system for decomposition (CEM Corp., USA) in the vessels LDV (pressure to 15 atm) and HDV (pressure to 40 atm). The temperature of solutions was monitored within 20—200 °C directly in vessels using a fiber-glass probe.

Investigation procedure. A weighed sample of an organic substance (0.1—0.4 g) was placed in an internal vessel of a 100-mL autoclave, 3—4 mL of concentrated HNO_3 and 0—1 mL of H_2O were added, and devices for pressure and temperature monitoring were connected. Then, the microwave system was switched-on (power 240—650 W), and the above-mentioned characteristics were measured at an interval of 5 s during 10—15 min. To calculate the activation energy (E_a) of oxidation, experimental points corresponding to a pressure change with temperature increase were chosen. The errors of pressure and temperature measurements were at most ±2%.

Results and Discussion

The processes that occur during oxidation of an organic compound with nitric acid under MW irradiation can simply be presented as the oxidation of some substance **A** with the formula $(\text{—CH}_2\text{—})_n$ through the sequential cleavage of carbon—carbon bonds.[1] The reaction affords carbon dioxide and water, which determine the pressure in the vessel.

$$(\text{—CH}_2\text{—})_n + 3n\,\text{O} \longrightarrow n\,\text{CO}_2 + n\,\text{H}_2\text{O} \qquad (1)$$

Let us consider the main relations determining the kinetics of the MW-enhanced chemical reaction in a closed vessel containing the liquid and gaseous phases. For rigid consideration, the model of the reaction kinetics in this system should take into account the dynamic micronononuniformity of the distributions of pressure, concentration, and temperature, which change in time. This requires to solve a complex system of equations in partial derivatives. However, processes under MW irradiation, unlike usual thermal heating in closed vessels (autoclaves), are characterized by high uniformity temperature and component concentrations in the solution at the macroscopic level. This fact makes it possible to use a simpler approximation that can be named a "uniform" model. Let us accept the following assumptions for this model: (1) pressure in the gas phase ($P(t)$) and concentrations of the reaction products in the liquid and gaseous phases ($c_{i,s}(t)$ and $c_i^*(t)$, respectively) are independent of the coordinates of a point in the reactor; (2) temperature ($T(t)$) in each time moment (t) is the same in the whole system; (3) fraction of the gas phase volume in the total reactor volume $\varepsilon = V_g/V_\Sigma$ changes slightly during the process; (4) pressure change in the gas phase with time is mainly determined by the occurrence of the chemical reaction.

The total pressure can be considered as the sum

$$P(t) = P^*(t) + P_0(t), \qquad (2)$$

where $P^*(t)$ is the pressure determined by gaseous products of the chemical reaction, and $P_0(t)$ is the total pressure determined by the starting components, which were in the gas phase before MW irradiation began to act, and equal to the sum of the corresponding partial pressures. A relation between the partial pressures and component concentrations can be expressed through the van der Waals equation. If we take for convenience the starting system of such a volume where the gas phase contains totally 1 mole of all components, we obtain

$$P_0(t) \approx RT(t)\sum_{i=1}^{n} x_{0i}\left(\frac{1}{V_g - x_{0i}b_i}\right) - \sum_{i=1}^{n}\frac{x_{0i}^2 a_i}{V_g^2} = RT(t)S_1 - S_2, \qquad (3)$$

$$dP_0/dt = RS_1(dT/dt), \qquad (4)$$

where x_{0i} is the molar fraction, a_i and b_i are the van der Waals constants for the ith component in the starting gas phase, and n is the number of components.

The pressure change during organic substance oxidation can be described by the equation

$$dP^*/dt = (\partial P^*/\partial t)_T + (\partial P^*/\partial T)_t \cdot (dT/dt), \qquad (5)$$

whose physical sense is that a small pressure shift in time in a nonisothermic process can be presented as the sum of contributions from the isothermic reaction and instant additional shift due to the temperature change in the reaction system.

Let us consider the temperature change in time (dT/dt) in the system where a chemical reaction occurs. The temperature is determined by both the MW absorption (dT_h) and the thermal effect of the reaction (dT_r), *i.e.*,

$$dT/dt = dT_h/dt + dT_r/dt.$$

The first term in the right part of this expression is proportional to the absorbed MW power, and the second term is proportional to the rate and thermal effect of the chemical reaction. This gives the correlation

$$\begin{aligned} dT/dt &= \{1/[\Sigma c_{v,i}m_i(t)]\}\cdot[\varpi + \lambda V_\Sigma \varepsilon(dc^*/dt)] = \\ &= S_3 + S_4(dc^*/dt), \qquad (6) \end{aligned}$$

where $c_{v,i}$ and $m_i(t)$ are the molar heat capacity and the number of moles of the ith component in the system; ϖ is the absorbed MW power; $c^*(t)$ is the molar concentration of one of the gaseous components, which is formed during the chemical reaction and whose content change in the system characterizes the chemical reaction rate (for example, CO_2 can be chosen as such a component); λ is the thermal effect of the chemical reaction referred to 1 mole of this forming component.

Let us analyze the ratio $(\partial P^*/\partial T)_t$ in Eq. (5) taking into account the van der Waals equation

$$P^* = c^*RT/(1 - bc^*) - a(c^*)^2.$$

Since certain difficulties appear in mathematical transformations of this expression, let us rewrite it as a function of an dimensionless magnitude

$$P^* = \sigma RT/(1 - \sigma) - \sigma^2/ab^2,$$

where $\sigma = bc^* \ll 1$, and expand in the series

$$\mathrm{d}P^*/\mathrm{d}\sigma = (\mathrm{d}P^*/\mathrm{d}\sigma)(0)\sigma + (\mathrm{d}^2P^*/\mathrm{d}\sigma^2)(0)(\sigma^2/2!) + \ldots$$

Neglecting all terms of the series with powers higher than unity, after inverse transformations we have

$$P^* \approx RTc^* + (RTb - a)(c^*)^2. \tag{7}$$

Verification using tables of numerical values of coefficients for carbon dioxide (a = 3.59 $\mathrm{L^2\,atm\,mol^{-2}}$, b = $4.27 \cdot 10^{-2}$ $\mathrm{L\,mol^{-1}}$)[9] shows that the deviation of Eq. (7) from the van der Waals equation at 30 atm and 373 K does not exceed 1%. When neglecting a change in the gas phase volume, time detection means concentration detection. Therefore, we can write

$$(\partial P^*/\partial T)_t = c^*R + (c^*)^2Rb \approx c^*R = \\ = \left(\frac{\sqrt{(RT)^2 + 4P^*(RTb - a)} - RT}{2(RTb - a)}\right)R = S_5R. \tag{8}$$

Let us analyze the ratio $(\partial P^*/\partial t)_T$ determining the reaction kinetics under isothermal conditions. For this purpose, simplified relation (7) is transformed to obtain

$$(\partial P^*/\partial t)_T \approx (\mathrm{d}c^*/\mathrm{d}t)\sqrt{(RT)^2 + 4P^*(RTb - a)} = \\ = (\mathrm{d}c^*/\mathrm{d}t)S_6. \tag{9}$$

Using Eqs (6), (8), and (9), we can write

$$\mathrm{d}P^*/\mathrm{d}t = S_6(\mathrm{d}c^*/\mathrm{d}t) + RS_5[S_3 + S_4(\mathrm{d}c^*/\mathrm{d}t)]. \tag{10}$$

Taking into account that

$$S_6 = \sqrt{(RT)^2 + 4P^*(RTb - a)} \approx RT,$$

in wide pressure (to 30 atm) and temperature (from 100 °C and higher) intervals with an accuracy not higher than percentage units and taking into account the equality

$$T = S_3t + S_4c^*,$$

which follows from the integration of Eq. (6) in the limits from 0 to t, the rate of gas pressure increase can be expressed through the concentration.

$$\mathrm{d}P^*/\mathrm{d}t = R(S_3t + S_4c^*)(\mathrm{d}c^*/\mathrm{d}t) + Rc^*[S_3 + S_4(\mathrm{d}c^*/\mathrm{d}t)] \tag{11}$$

Let us consider different conditions for chemical reactions of oxidation of organic substances in a closed volume under MW irradiation.

Pseudo-first-order reactions. Starting substance **A** is oxidized in solution in an excess of an oxidizing agent (for instance, in the case of water-soluble substances, such as saccharose, amino acids, and other). The rate of concentration increase for any gaseous reaction product can be expressed as follows:

$$\mathrm{d}c^*/\mathrm{d}t = -\mathrm{d}[\mathbf{A}]/\mathrm{d}t = k_1[\mathbf{A}], \tag{12}$$

where k_1 is the rate constant.

The well-known equations follow from relation (12)

$$\mathrm{d}c^*/\mathrm{d}t = k_1[\mathbf{A}]_0\exp(-k_1t),\ c^* = [\mathbf{A}]_0[1 - \exp(-k_1t)], \tag{13}$$

where $[\mathbf{A}]_0$ is the starting concentration of the reactant in solution.

For low conversions ($[\mathbf{A}] \approx [\mathbf{A}]_0$),

$$c^* = [\mathbf{A}]_0k_1t,\ \mathrm{d}c^*/\mathrm{d}t = [\mathbf{A}]_0k_1. \tag{14}$$

It follows from Eqs (11) and (14) that

$$\mathrm{d}P^*/\mathrm{d}t \approx 2R[\mathbf{A}]_0k_1(S_3 + S_4k_1)t. \tag{15}$$

Integration of the latter taking into account the integral of Eq. (6) gives the expression

$$P^* \approx \mathrm{const}[\mathbf{A}]_0RTk_1t. \tag{16}$$

If several gaseous products are formed instead of one, the form of relation (16) remains unchanged but the value of the coefficient in the right part changes. Therefore, Eq. (2) can be written in the form

$$P(t) \approx P_0(t) + \mathrm{const}^*[\mathbf{A}]_0RTk_1t. \tag{17}$$

Using Eqs (6), (12), (16), and (17) and accepting that at any temperature the pressure in the gas phase appeared due to the chemical reaction is much higher than the pressure that would be in the absence of the chemical reaction, *i.e.*, $P(t) \gg P_0(t)$, we have

$$\mathrm{d}(\ln P)/\mathrm{d}T \approx \mathrm{d}(\ln k_1)/\mathrm{d}T + \mathrm{d}(\ln t)/\mathrm{d}T + \mathrm{d}(\ln T)/\mathrm{d}T = \\ = E_a/(RT)^2 + 1/T + 1/[(S_3 + S_4k_1)t] = \\ = E_a/(RT)^2 + 2/T. \tag{18}$$

Taking into account that for chemical reactions the activation energy is usually higher than $3 \cdot 10^4$ J $\mathrm{mol^{-1}}$, we can write instead of Eq. (18)

$$\mathrm{d}(\ln P)/\mathrm{d}T \approx \mathrm{d}(\ln k)/\mathrm{d}T = E_a/(RT)^2. \tag{19}$$

Thus, for pseudo-first-order reactions, the dynamic method for determination of the activation energy can be used in the initial region of the curve of pressure increase.

Zero-order reaction (topochemical reaction). The most part of reactions of oxidative combustion of an insoluble organic substance correspond to zero-order reactions.

For the zero-order reaction

$$dc^*/dt = k_0. \qquad (20)$$

Evidently, conditions (16) and (19) are fulfilled up to chemical reaction completion, *i.e.*, in the whole region of pressure increase.

Second-order reaction. The reaction rate depends on both the concentration of the soluble oxidized organic substance and oxidizing agent concentration

$$dc^*/dt = k_2[\mathbf{A}]c^*. \qquad (21)$$

It is easy to show that conditions (16) and (19) do not hold and, hence, the dynamic method for determination of the activation energy cannot be used in the proposed form.

Taking into account all obtained results, we can write the mathematical model for the MW-enhanced change in the temperature and pressure in the reaction system.

$$\begin{cases} T(t) = T_0 + \{1/[\Sigma c_{v,i} m_i(t)]\} \cdot (\varpi + \lambda V_\Sigma \varepsilon k)t \\ P(t) = P_0 + \mathrm{const} RT(t)t \\ k_T = k_{T_0} \exp\{(E_a/R) \cdot [(1/T_0) - (1/T)]\} \end{cases} \qquad (22)$$

It is seen that the time dependence of the temperature is close to linear, while the pressure (in the region of increasing) changes approximately proportionally to the squared time.

The experimental curve of the temperature and pressure change for the MW-enhanced oxidation of phenylalanine are presented in Fig. 1.

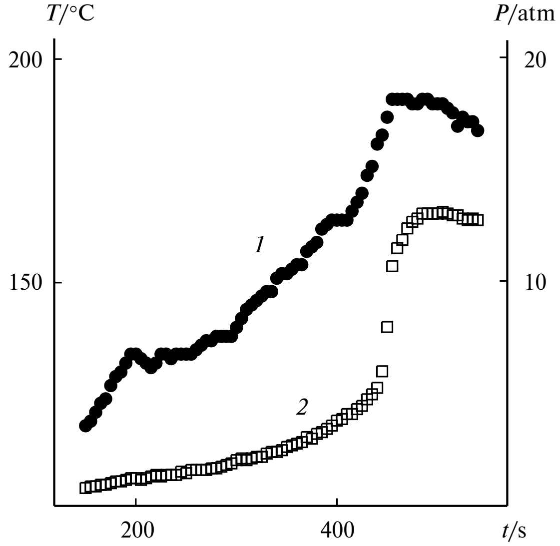

Fig. 1. Effect of microwave heating on the change in the temperature (*1*) and pressure (*2*) in a closed vessel for phenylalanine oxidation with nitric acid.

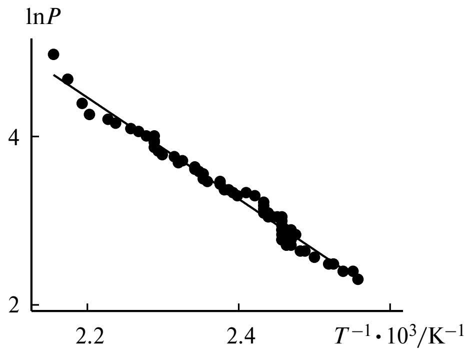

Fig. 2. Arrhenius plot for the pressure *vs.* temperature for phenylalanine oxidation with nitric acid under microwave irradiation (E_a = 50.1 kJ mol^{-1}).

Table 1. Activation energy (E_a) of oxidation of organic compounds with nitric acid

Compound	E_a/kJ mol^{-1}	
	Experiment*	Literature data
Phenylalanine	50.1	50.0 [10]
Trypthophan	32.0	29.8 [10]
Oxalic acid	120	120 [11]

* Determined under microwave heating.

Since at this level the model includes empirical parameters, we cannot say that the theoretical curves coincide with experimental results but they are evidently similar.

An example for the determination of the activation energy using the above-substantiated dynamic method is shown in Fig. 2. The results obtained by a similar method for several oxidation processes are given in Table 1. A comparison with the published data[10,11] suggests that the values obtained by the proposed method are reliable.

Briefly summarizing the above-presented data, we can conclude that the dynamic method based on an analysis of the experimental exponential dependence of the total pressure in the system on the inverse temperature of the reaction mixture can be used to estimate the activation energy of MW-enhanced oxidation processes at the chosen approximations that include the assumption about the zero or pseudo-first reaction order.

The data presented substantiate a possibility of using MW heating for the efficient influence on physicochemical processes in solutions and heterogeneous systems and also for the fast determination of quantitative characteristics of reactions.

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