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Functional Relationships Between Kinetic, Flow, and Geometrical Parameters in a High Temperature Chemical Micro-Reactor

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Abstract. A resistively-heated silicon carbide high-temperature ‘chemical reactor’ (micro-reactor) incorporated into a molecular beam apparatus operated with a Wiley-McLaren reflectron time-of-flight mass spectrometer (Re-TOF-MS) was employed for experimental studies of pyrolysis of 1- and 2-bromonaphthalene. Computational fluid dynamics (CFD) simulations and isothermal approximation were applied for the interpretation of experimental measurements of the C₁₀H₇Br pyrolysis efficiency in the high-temperature micro-reactor and of the pressure drop in the flow tube of the reactor. Applying isothermal approximation allows the derivation of analytical relationships between the kinetic, gas flow, and geometrical parameters of the micro-reactor which, along with CFD simulations, accurately predict the experimental observations. Based on the obtained analytical relationships, a clear strategy for measuring rate coefficients of (pseudo-)first-order bimolecular and unimolecular reactions using the micro-reactor has been proposed. The pressure- and temperature-dependent rate coefficients for the C₁₀H₇Br pyrolysis calculated using variable reaction coordinate transition state theory (VRC-TST) were invoked to interpret the experimental data on the pyrolysis efficiency.
1. **Introduction**

Experimental measurements of kinetic rate constants for chemical reactions relevant to combustion processes under typical combustion conditions represent a key challenge for accurate modeling and proper understanding of fuel burning. Only a few percent of combustion reaction rate constants have been measured at the temperatures inherent to combustion. This is due to the insufficient development of experimental instrumentation to carry out kinetic measurements at high temperatures and pressures. A high temperature silicon carbide (SiC) chemical micro-reactor incorporated with photoionization mass spectrometry (PIMS) provides an opportunity to measure the kinetic constants of processes under high-temperature conditions up to 2000 K.\(^1\)\(^-\)\(^9\)

However, several deficiencies of the high-temperature micro-reactor complicate the interpretation of the experimental data. First, gas acceleration and friction against the micro-reactor walls at transonic velocities result in a significant pressure drop and a velocity increase along the flow in the reactor’s tube. Second, the wall temperature of the reactor is generally not uniform. Under these conditions, finding dependences of the relative number densities of the reactants and products at the reactor’s exit on the residence time of the gas mixture and the number of collisions in the reaction zone is not a simple task. At present, complex computational fluid dynamics (CFD) simulations in the channel of the micro-reactor accounting for the conservation of mass, momentum balance of the viscous flow, and the heat transfer have been applied to interpret the experimental data\(^1\),\(^6\) and to extract the kinetic information.

Guan et al.\(^1\) carried out CFD simulations to explore the gas flow and chemical processes in a micro-reactor in detail. Their analysis of the CFD simulation results has shown that the micro-reactor exhibits several characteristic features in the behavior of the gas flow and its interplay with the chemical kinetics of the reactions involved including the following: a) the gas flow in the reactor is laminar; b) the gas velocity reaches the sonic speed at the exit of the reactor’s channel; c) there is a slip of the flow at the boundaries near the downstream end of the reactor under some circumstances; d) the influence of secondary chemical reactions can be minimized. Guan et al.\(^1\) illustrated that the CFD simulation results are comparable with the observed experimental data and concluded that the kinetic information can be extracted by matching CFD simulations with the concentrations of the reactant and product measured at the reactor’s exit.

The CFD simulation provides a great deal of information on distributions of temperature, pressure, velocity, and number densities of the reacting species along the gas flow in the micro-reactor. The results of numerical simulations presented in the literature\(^1\),\(^5\) show that these
distributions may vary dramatically. Fluid dynamic equations take into account both principal and minor interactions and therefore the calculated concentrations of the reactant and product at the reactor’s exit depend in a complex manner on the parameters of the reactor and the gas flow. Then, a question arises: Do other strategies exist besides the CFD simulation that can be used to evaluate kinetic constants based on the experimental results measured? When measuring kinetic constants of chemical reactions, handy dependences of the residence time and the number of collisions between reacting species on the flow and the reactor parameters are very much in demand. Finding such dependences would greatly simplify the interpretation of experimental measurements and would allow one to select optimal parameters of the gas flow and the reactor.

In the present work, we engage isothermal approximation to derive the dependences of the residence time, the number of collisions, and the output fractions of the components of interest on the flow and reactor parameters in an explicit, analytical form. CFD calculations and flow tube and PIMS measurements are then invoked to validate the obtained analytical dependences by conducting calibration experiments for nitrogen (N₂), oxygen (O₂), carbon dioxide (CO₂), ethylene (C₂H₄), and helium (He). Finally, the developed theoretical expressions are exploited to extract the rate coefficient for unimolecular decomposition of 2-bromonaphthalene (2-C₁₀H₇Br) from its output fraction measured experimentally and the results are compared with CFD simulations and with purely theoretical calculations using variable reaction coordinate transition state theory (VRC-TST).

2. Experimental
2.1. High temperature micro-reactor coupled with photoionization mass spectrometry

A resistively-heated silicon-carbide (SiC) high-temperature ‘chemical reactor’ (T = 1500 K) incorporated into a molecular beam apparatus operated with a Wiley-McLaren reflectron time-of-flight mass spectrometer (Re-TOF-MS) was employed for experimental studies of pyrolysis of 2-bromonaphthalene.¹⁰,¹¹ The micro-reactor represents a gas-flow SiC tube with an internal diameter of 1 mm, total length of 38 mm, and ohmic heating zone length of 20 mm. The temperature of the SiC tube was monitored using a type-C thermocouple. A simplified sketch of the micro-reactor is shown in Figure 1. The inlet end of the SiC tube was inserted into a hole in the alumina holder, which in turn was surrounded by a copper heat-exchanger cooled by water. Molybdenum electrodes with a diameter of 21 mm and a width of 4 mm come into contact with the SiC tube through graphite slivers. The carrier gas and pyrolysis products flow into the zone of strong rarefaction (pressure below 10⁻⁶ torr). After exiting the pyrolytic reactor, the molecular
beam passes a skimmer and enters a detection chamber containing a ReTOF mass spectrometer. The products were photoionized in the extraction region of the spectrometer by exploiting quasi continuous tunable vacuum ultraviolet (VUV) light from the Chemical Dynamics Beamline of the Advanced Light Source and detected with a microchannel plate detector. The gases used in the experiments had the following purities as stated by the manufacturers: He (99.9999 %; Airgas) and 2-C_{10}H_{7}Br (99.9 %+, Aldrich). The experiments with the SiC micro-reactor were performed under the conditions presented in Table 1.

2.2. Gas-flow testing line

The gas scheme used for measuring the pressure drop in the tube of the SiC chemical reactor is presented in Figure 2. A Mass-Flow Controller (MFC) GE50A with 200 sccm nitrogen (N\_2) full range governed from a personal computer (PC) was used to control the mass flow rate. The Baratron pressure gauge (Model 722A-23274) measured the gas pressure \( P_{in} \) upstream of the tube. Another 275 Convectron Pirani vacuum gauge measured the gas pressure \( P_{ex} \) downstream from the tube. Then gas channel in the tube with 1.0 mm inner diameter and 2 cm length was drilled in the 9.5 mm steel cylinder. The gas duct was pumped out with TriScroll vacuum pump (Model TS300). The valves V\_1, V\_2, and V\_3 served for redirection of the gas flow or/and separation of some part of the flow from the others. The UHP sample gases oxygen (O\_2), carbon dioxide (CO\_2), ethylene (C\_2H\_4), and helium (He) were used.

3. Calculations of the rate coefficient for the pyrolysis of C\_10H\_7Br

To evaluate the high-pressure limit (HP) rate constants for the barrierless reactions of the Br atom with 1- and 2-naphthyl radicals C\_10H\_7, we employed variable reaction coordinate transition state theory VRC-TST.\textsuperscript{12,13} Within this framework, we computed \((E,J)\)-resolved reactive flux for the Br addition to C\_10H\_7. The data obtained were then converted to macrocanonical temperature-dependent HP rate constants, which in turn were utilized in master equation calculations of pressure dependence. Energies of various structures were probed at the CASPT2(2,2)/cc-pVDZ level of theory,\textsuperscript{14,15} where the active space included one unpaired electron of the bromine atom, one unpaired electron of the naphthyl radical C\_10H\_7 and the two corresponding orbitals. Then, the following \textit{ad hoc} one-dimensional corrections depending only on the \( R_{CBBr} \) distance corresponding to the forming C–Br bond were included:

\[
E_{rel}[\text{Method}] = E_{rel}[\text{CASPT2}(2,2)/\text{cc} - \text{pVDZ}] + \Delta E[\text{geom}] + \Delta E[\text{Method}]
\]
where $E_{\text{rel}}$ is a relative energy for a particular Br/C$_{10}$H$_7$ configuration with respect to the separated Br + C$_{10}$H$_7$ fragments. $\Delta E[\text{geom}]$ is a correction for geometry relaxation computed as a difference of energies of an optimized structure along the minimum energy path (MEP) for the approaching fragments corresponding to a particular value of $R_{\text{CBr}}$ and the structure at the same $R_{\text{CBr}}$ but with geometry of the C$_{10}$H$_7$ fragment frozen (the same as in an isolated C$_{10}$H$_7$ radical). The calculations of $\Delta E[\text{geom}]$ were carried out at the CASPT2(2,2)/cc-pVDZ level. The geometry optimization was not complete because all the dihedral angles were kept frozen at 0° or 180° to ensure $C_s$ symmetry of the structure. $\Delta E[\text{Method}]$ is a correction for a higher level of theory computed for frozen-fragment structures along the MEP also corresponding to particular values of $R_{\text{CBr}}$:

$$\Delta E[\text{Method}] = E_{\text{ref}[\text{Method}]} - E_{\text{ref}[\text{CASPT2(2,2)/cc-pVDZ}]}$$

The higher-level corrections were evaluated at the CASPT2 level with the same (2,2) active space and the cc-pVTZ ($E_{\text{cc-pVTZ}}$) and cc-pVQZ ($E_{\text{cc-pVQZ}}$) basis sets. The calculated values were then used for extrapolation to the complete basis set (CBS) limit using the two-point expressions

$$E_{\text{CBS}} = E_{\text{cc-pVQZ}} + (E_{\text{cc-pVQZ}} - E_{\text{cc-pVTZ}}) \times 0.69377$$
$$E_{\text{CBS}} = E_{\text{cc-pVTZ}} + (E_{\text{cc-pVTZ}} - E_{\text{cc-pVDZ}}) \times 0.46286$$

The corrections were computed at finite values of $R_{\text{CBr}}$ between 1.6 and 8 Å and then an interpolation by splines was employed to evaluate the corrections at arbitrary $R_{\text{CBr}}$ values within the given range. All the ab initio calculations were performed using the GAUSSIAN 09$^{16}$ and MOLPRO 2010$^{17}$ program packages.

On the course of VRC-TST calculations, the corrections were added to the explicitly computed energy of a configuration based on the $R_{\text{CBr}}$ value in this configuration. In the case of 1-bromonaphthalene (Figure 3), there was only small difference between two values obtained using the aforementioned expressions at lengths from the range of interest ($R_{\text{CBr}} \approx 1.9$ Å and higher in the C$_{10}$H$_7$Br molecules), so the extremely demanding computations with the cc-pVQZ ($E_{\text{cc-pVQZ}}$) basis set were not carried out for 2-bromonaphthalene. Bond dissociation energies used in ME-analysis were set to 81.2 kcal/mol and 81.7 kcal/mol for 1- and 2-bromonaphthalene respectively.$^{18}$ Calculated rate constants for unimolecular dissociation of 1- and 2-bromonaphthalene to C$_{10}$H$_7$ + Br are presented in Figure 3.

Rate constant values were approximated by modified Arrhenius expressions and used in numerical simulations. The list of reactions significant for the modeling of the 2-C$_{10}$H$_7$Br pyrolysis is presented in Table 2. The pressure dependence of $k_{1f}$ was approximated as logarithmic. Rate constants of the secondary reactions 2 and 3 were taken from the literature.$^{19,20}$
4. Results and Discussion

4.1. CFD simulation results

In this section, we present the velocity, pressure, temperature and reactive species distributions in the reactor computed by solving the Navier-Stokes equations for the conservation of mass, momentum balance for the viscous flow, and the heat transfer reported elsewhere.\textsuperscript{1,6,8} Usually, in experiments the reactive species were greatly diluted with a carrier gas and so we can ignore the effect of chemical reactions on the dynamics of the flow. The Comsol-Multiphysics package\textsuperscript{21} was employed for the calculation of the distribution of gas-dynamic parameters of the gas flow in the micro-reactor. When simulating physicochemical processes in the micro-reactor, the following tasks were simultaneously solved: the flow of the electric current and ohmic heating, the heat transfer between the nodes of the micro-reactor and the radiative heat transfer to the surrounding space, the Navier-Stokes and heat-mass transfer problems in the gas flow, the kinetics of the pyrolysis process. The temperature dependences of the viscosity, heat conductivity, and heat capacity in the range of $T = 300$-$1600$ K were taken into account. For the mass flow used, the gas pressure closer to the exit of the reactor can be less than 10 Torr. Under these conditions with the He carrier gas there is a slip of the flow at the boundaries.\textsuperscript{1,6} This phenomenon was taken into account within the boundary conditions. The initial data for the calculations are presented in Table 1.

The ohmic heating power was adjusted so that to achieve the reactor wall temperature of about 1500 K at the point between the electrodes. The heat power of 37 W is mainly lost via radiative emission (33 W) from the SiC tube, graphite slivers, and molybdenum electrodes. A small part (3 W) of the heat power leaks through the alumina holder. The rest of the heat (1W) is carried away with the gas flow. Thus, the ohmic heating and the heat transfer tasks were solved first without solving the momentum and mass conservation tasks and the heat transfer in the gas phase. The last three tasks were solved in the following manner. The static inlet pressure and pressure in the gas stream at the outlet were fitted to provide the mass flow rate and the sonic gas velocity at the outlet. The Maxwell model for the slip velocity boundary conditions at the wall of the reactor was employed. The distributions of temperature $T$, pressure $P$, and gas velocity $U_0$ along the tube at the central axis of the reactor are presented in Figure 5. Analogous modeling was also performed at the electric power of 48 W at which the micro-reactor’s temperature was 1600 K. Calculations show that the distributions of the radial temperature and number densities of the gas components are almost uniform in the high-temperature region of the reactor.
The temperature distribution in the SiC reactor between the electrodes is determined from the balance of the energy input during the resistive heating and energy removal both during the heat transfer along the tube and thermal radiation from the surface of the tube and electrodes. Figure 5 displays the temperature dependence for the SiC tube with the assumed heat conductivity $\lambda = 12 \text{ W m}^{-1} \text{ K}^{-1}$, $T = 1500 \text{ K}$ (solid curve), whereas the dashed curve shows the temperature distribution for a ZrO$_2$ tube with $\lambda = 2 \text{ W m}^{-1} \text{ K}^{-1}$. Clearly, in the case of a ZrO$_2$ tube, the reactor temperature is nearly uniform along almost the entire interval of the tube between the electrodes that should be conducive for measuring kinetic constants in the reactor.

CFD calculations of pressure $P$, temperature $T$ and axis velocity $U_0$ distribution as well as the rate constants presented in Table 2 (including those for forward and reverse $2\text{C}_{10}\text{H}_7\text{Br} \rightarrow \text{C}_{10}\text{H}_7 + \text{Br}$ reactions computed here) were used to compute the $2\text{C}_{10}\text{H}_7\text{Br}$ pyrolysis efficiency for two wall temperatures of the SiC tube between electrodes. The results of the calculations are presented in Figure 6. According to the results, the pyrolysis efficiency of 2-bromonaphthalene was about 15% at 1500 K and 46% at 1600 K. One has to take into account the accuracy of the rate constant estimation and the accuracy of the micro-reactor’s temperature measurements. Taking these points into account, we can conclude that the experimental result (40%) is in good agreement with the results of calculations of the pyrolysis efficiency (15-46%). The pressure drop and the velocity increase together with the temperature decrease along the flow at $z \geq 2.8$ cm causes the pyrolysis process to stop as can be seen from the results presented in Figure 6. We can also see from this Figure that the pyrolysis of $2\text{C}_{10}\text{H}_7\text{Br}$ occurs in the range from $z_1 = 18$ mm to $z_2 = 28$ mm. In this reaction zone the gas temperature varies within narrow limits $T \approx 1450\div1500 \text{ K}$. The average residence time calculated using the equation derived previously (Eq. S7 in Ref. 6) at the experimental conditions ($T = 1500 \text{ K}$) in the $z$-interval [18 mm, 28 mm] of the reactor amounts to $\tau_{res} = 56 \mu\text{s}$.

These CFD calculations illustrate that the rate constant for the $2\text{C}_{10}\text{H}_7\text{Br}$ pyrolysis can be derived from the measured pyrolyzed fraction of $\text{C}_{10}\text{H}_7\text{Br}$ at the exit of the reactor by matching the simulation result to experiment achieved through adjustment of the assumed rate constant expression; here, the assumed rate constant expression was obtained from the first-principles VRC-TST calculations. It should be also noted that the result for the pyrolysis efficiency in the present case appears to be not sensitive with respect to the assumed rate constants for the secondary reactions of the formation and dissociation of Br$_2$. In the consequent Section, we consider how the rate constant can be evaluated more directly, without CFD simulations.

4.2. Isothermal approximation
Acceptable accuracy in measurements of kinetic constants having strong temperature dependence can be attained if the temperature between electrodes is close to uniform. The CFD calculation results show that this can be achieved by using the material for the tube of the reactor with low thermal conductivity and with an appropriate design of the electrodes. In this case, the chemical reaction under consideration would take place under nearly uniform conditions and one can obtain rather simple and clear dependences of the residence time and the number of collisions in the reaction zone on the parameters of the reactor and the gas flow using the following assumptions:

- The gas flow is laminar and isothermal;
- There are no pressure and temperature gradients across the flow (fast heat and momentum transverse transport);
- Number density of each component is uniform across the flow (fast transverse diffusion);
- The velocity profile across the flow is parabolic throughout the reactor length;
- The centerline gas velocity at the outlet edge of the reactor is sonic;
- There is no slip of the gas stream at the surface of the reactor.

Then, the gas mass flow rate \( g \) can be expressed as

\[
g = dy \int_0^\gamma 2\pi y U(z) \frac{P(z)}{RT} \left( 1 - \frac{2y}{d} \right)^2 dy = \frac{sP(z)U(z)}{2RT} \quad (1)
\]

Here, \( U \) is the centerline axial velocity, \( P(z) \) is the gas pressure at distance \( z \) from the inlet edge of reactor, \( R(J kg^{-1} K^{-1}) = 8.31/M \) is the gas constant, \( M(kg /mol) \) is the molecular weight of the gas mixture, \( s = \pi d^2/4 \) is the cross-section of the gas channel, \( d \) is the internal tube diameter, and \( T \) is the gas temperature. In particular, the pressure of the gas at the reactor exit is equal to

\[
P_{out} = \frac{2gR}{sc} = \frac{2gc}{\gamma s}, \quad (2)
\]

where \( c = \sqrt{\gamma RT} \) is the sonic velocity at temperature \( T \) and \( \gamma \) is the heat capacity ratio.

The total momentum \( I \) of the gas stream can be found as follows

\[
I = \int_0^\gamma 2\pi y \left( P(z) + \frac{U^2(z)P(z)}{RT} \left( 1 - \frac{2y}{d} \right)^2 \right) dy = P(z)s \left( 1 + \frac{U^2(z)}{3RT} \right) \quad (3)
\]

The pressure drop is due to the viscous force at the surface, which is equal to \( 4\pi U_0 \mu \) per unit of length along the tube. Then, one obtains the equation for the momentum

\[
\frac{dl}{dz} = -4\pi \mu U, \quad (4)
\]
where $\mu$ is the viscosity coefficient. Taking into account Eqs. (1)-(3), the solution of the differential equation (4) is given by

$$P(z)^2 - P_{out}^2 \left(1 + \frac{4\pi \gamma \mu}{g} \right) - \frac{2y^2 P_{out}^2}{3} \ln \left(\frac{P(z)}{P_{out}}\right) = 0,$$

where $L$ is the total length of the reactor. Using Eqs. (2) and (5) together, we can find the pressure distribution $P(z)$ along the flow in the reaction zone. In practically interesting cases, the condition $\frac{4\pi \gamma \mu L}{g} >> 1$ is valid. In this case, Eq. (5) can be rewritten as follows

$$P(z) = P_{out} \sqrt{1 + \frac{4\pi \gamma \mu (L-z)}{g}} = \frac{2gR \cdot T}{s^c} \sqrt{1 + \frac{4\pi \gamma \mu (L-z)}{g}}$$

(6)

It follows from Eq. (6) that the gas pressure at the inlet of the reaction zone ($z = 0$) is given by

$$P_{in} = \sqrt{\left(\frac{gR \cdot T}{0.5s^c}\right)^2 + \frac{16\mu \cdot R \cdot T \cdot \pi \cdot gL}{s^2}}$$

(7)

The assumptions made above can be critical for finding target parameters under conditions of transonic velocities at low outlet pressures. In this Section we present experimental and CFD calculated results proving that isothermal approximation can be applied for finding relationships between the flow and the reactor parameters. Using the gas-flow testing line shown in Fig. 2, the inlet gas pressures ($z = 0$) were measured in relation to the molar flow rates of CO$_2$ and He at ambient temperature which are depicted with black square symbols in Figures 7 and 8. Blue triangle symbols in these Figures represent the results of CFD simulations at the experimental conditions. Finally, red circles show the input pressures calculated using Eq. (6) obtained within isothermal approximation. The calculations utilized the dependences of viscosity coefficients and adiabatic constants on the gas temperatures shown in Table 3. One can see that both CFD and analytical calculations satisfactory reproduce the experimental data in the wide range of variation of the gas flow rate of O$_2$, C$_2$H$_4$, CO$_2$, and He. This testifies to the validity of our assumptions adopted in the beginning of this Section.

Typical pressure distributions along the flow calculated using Eqs. (5) and (6) along with CFD simulations are exhibited in Figure 9 at $T = 1500$ K and the molar flow rate $g = 400$ sccm for two carrier gases C$_2$H$_4$ and He. CFD calculations were carried out at a constant temperature of the reactor wall, although the gas temperature closer to the outlet of the reactor was slightly decreased. The differences between the three calculated pressure distributions do not exceed 10% all the way from the entrance to the exit of the reaction zone. The lighter the carrier gas and the lower the gas flow rate, the higher the ratio $\varepsilon = P_{in}/P_{out}$. For example, for the conditions of
Fig. 9, the values of $\varepsilon$ amount to 1.57 and 5.24 for C$_2$H$_4$ and He, respectively. For $g = 50$ sccm and $T = 1500$ K, the values of $\varepsilon$ are 3.2 and 16.9 for C$_2$H$_4$ and He, respectively. Thus, the most uniform pressure distribution can achieved with heavier carrier gases at higher flow rates but the latter condition represents a technical challenge.

As mentioned above, the pressure distributions calculated by CFD and via Eqs. (5) and (6) are very similar. At isothermal conditions this means that the average velocity distributions along the $z$ axis are also very similar. The distribution from Eq. (6) exhibits a clear analytical dependence on the reactor and gas flow conditions. Therefore, the use of Eq. (6) allows us to obtain a clear analytical dependence of the most important parameters such as the gas residence time, the number of collisions of a molecule with ambient molecules, and the consumption of reacting components. It is more convenient to derive the formulas of interest using the distance from the outlet of the reactor $y = L - z$. The gas residence time inside the interval $[y_1, y_2]$ in isothermal approximation can be expressed as follows

$$
\tau_{\text{res}}(y_1, y_2) = \int_{y_1}^{y_2} \frac{p(y) s}{gRT} dz = \frac{2}{\varepsilon} \cdot \sqrt{1 + \frac{4\pi\mu y}{g} dy}
$$

(8)

where $y = L - z$, $y_1 = L - z_1$, $y_2 = L - z_2$ are distances from the reactor outlet and $y_1 > y_2$. Substitution of Eq. (6) into Eq. (8) and integration of the resulting expression gives an analytical formula for the residence time

$$
\tau_{\text{res}}(y_1, y_2) = \frac{g}{3\pi c y \mu} \left(1 + \frac{4\pi\mu c^2}{gR T} y_1^{1.5} - \left(1 + \frac{4\pi\mu c^2}{gR T} y_2^{1.5}\right)^\mu\right)
$$

(9)

Taking into account that $c = \sqrt{y RT}$ one obtains

$$
\tau_{\text{res}}(y_1, y_2) = \frac{g}{3\pi y^{1.5(RT)} \mu} \left[1 + \frac{4\pi\mu y}{g} y_1^{1.5} - \left(1 + \frac{4\pi\mu y}{g} y_2^{1.5}\right)^\mu\right]
$$

(10)

It is remarkable that there is no dependence of the residence time on the reactor diameter $d$. Using Eq. (10) the dependences of residence time $\tau_{\text{res}}$ on the gas temperature $T$, the interval $(y_1, y_2)$ of the reaction zone, the gas flow rate $g$, and the molecular weight of the gas mixture $M$ can be easily traced. To calculate the total gas residence time in the reactor one has to make a substitution $y_1 = L$, $y_2 = 0$ in Eq. (10).

The dependences of the residence time on the gas flow rates of He, C$_2$H$_4$, and CO$_2$ with the reaction zone length $L = 1$ cm and the gas temperature of 1000 K are shown in Figure 10 as an example. As can be seen, a fast decrease in the residence time with the gas flow rate occurs for the gas flow rates below 100 sccm and then the residence time drops only moderately at higher values of the flow rate. For instance, with an increase in the gas flow rate from 200 to 400
seem \( \tau_{\text{res}} \) falls by only about 20%. Using He as a carrier gas is preferable because this allows one to obtain lowest values of the residence time. The residence time calculated using Eq. (10) for the interval \([y_1 = 2 \text{ cm}, y_2 = 1 \text{ cm}\) or \(z_1 = 1.8 \text{ cm}, z_2 = 2.8 \text{ cm}\) at the experimental conditions for the 2-C\(_{10}\)H\(_7\)Br pyrolysis, \(T = 1500 \text{ K}\), \(g = 2.46 \times 10^{-4} \text{ g/s}\), \(\mu = 4.4 \times 10^{-4} \text{ g/(cm s)}\) amounts to \(\tau_{\text{res}} = 67 \mu\text{s}\), in satisfactory agreement with the CFD calculated result.

The number of collisions of reacting species is one of important parameters necessary for evaluating kinetics constants. Using the known distribution of the gas pressure determined by Eq. (6), the number \(N\) of collisions of a selected molecule with ambient molecules in the interval \([y_1, y_2]\) zone is given by

\[
N(y_1, y_2) = k \int_{\tau_{\text{res}}(x_1)}^{\tau_{\text{res}}(x_2)} n \, d\tau_{\text{res}} = k \frac{4g(y_1-y_2)}{g_k B T_s} \left[ 1 + \frac{2\gamma \pi \mu}{g} (y_1 + y_2) \right],
\]

where \(k\) is a rate constant in the gas-kinetic collision limit \((-10^{-10} \text{ cm}^3/\text{s})\), \(n = \frac{P(y)}{k_B T}\) is the total number density, \(k_B\) is Boltzmann constant. For example, at the experimental conditions for the 2-C\(_{10}\)H\(_7\)Br pyrolysis the calculations give the number of collisions \(N = 708\) in the interval \([2 \text{ cm}, 1 \text{ cm}]\).

Finally, let us derive the expressions that relate the fraction of a component A reacting in a bimolecular reaction \(A + B\) having rate constant \(k_{AB}\) in a carrier gas \(C\). The subject of interest is a change of the value \(\eta_A = n_A/n\) at when gas flows from the distance \(z_1\) \((z_1 = L - y_1)\) to the distance \(z_2 = L - y_2\) in the reactor. Here \(n_A\) and \(n_C\) denote the number densities of the component A and the carrier gas, respectively. It is assumed that numbers density of the components A, B and C are in the relation \(n_C \gg n_B \gg n_A\). The balance rate equation for a pseudo-first order bimolecular reaction \(A + B\) under our assumptions has the following form

\[
-\frac{d}{dz} \eta_A = \frac{d}{dy} \eta_A = k_{AB} (\eta_B n) \left( \eta_A n \right) \frac{M_s}{N_A g},
\]

where \(\eta_B = n_B/n\), \(n = n_A + n_B + n_C\), \(N_A\) is Avogadro number. The solution of Eq. (12) is given by

\[
\ln \frac{\eta_A(y_2)}{\eta_A(y_1)} = -\frac{k_{AB} n_B M_s}{g N_A} \int y_1 \left( \frac{P(y)}{k_B T} \right)^2 dy
\]

By integrating Eq. (13) we obtain the following expression relating the fraction of the component A to the parameters of the reactor and the gas flow within the distance from \(y_1\) to \(y_2\)

\[
\frac{\eta_A(y_2)}{\eta_A(y_1)} = \exp \left( -\frac{k_{AB} n_B N(y_1,y_2)}{k} \right) = \exp \left\{ -k_{AB} n_B \frac{4g(y_1-y_2)}{g_k B T_s} \left[ 1 + \frac{2\gamma \pi \mu}{g} (y_1 + y_2) \right] \right\}
\]

where \(N(y_1,y_2)\) is defined by Eq. (11).
For a unimolecular reaction $AB \rightarrow A + B$ with a pressure independent rate coefficient $k_{AB} \text{ (s}^{-1})$ the change of the AB fraction in the interval $[y_1, y_2]$ is

$$\frac{\eta_A(y_2)}{\eta_A(y_1)} = \exp(-k_{AB} \tau_{res}(y_1, y_2)) =$$

$$= \exp \left\{ -\frac{k_{AB} y}{3\pi y^{1.5}(R T)^{0.5} \mu} \left[ \left(1 + \frac{4\pi \mu y_1 y}{g}ight)^{1.5} - \left(1 + \frac{4\pi \mu y_2 y}{g}ight)^{1.5} \right] \right\} \quad (15)$$

Let us estimate the efficiency of 2-C$_{10}$H$_7$Br decomposition using Eq. (15). We assume that pyrolysis occurs only within the distance interval $z_1 = 1.8 \text{ cm}$ ($y_1 = 2 \text{ cm}$) to $z_2 = 2.8 \text{ cm}$ ($y_2 = 1 \text{ cm}$) and the temperature is 1500 K. This assumption is reasonable because COMSOL calculations showed explicitly that efficient decomposition of 2-C$_{10}$H$_7$Br occurs in this interval (see Fig. 6). The calculation with the numerical values of the viscosity $\mu = 4.44 \times 10^{-4} \text{ g cm}^{-1} \text{ s}^{-1}$ (Table 1), the rate constant of 2-C$_{10}$H$_7$Br decomposition $k_{AB} = k_{fP1} = 1.52 \times 10^3 \text{ s}^{-1}$ at $T = 1500 \text{ K}$ (Table 2) gives $\frac{\eta_A(y_2)}{\eta_A(y_1)} = 0.90$ or the efficiency of decomposition of 10%. This is in good agreement with the CFD-calculated result 13% (Fig. 6), but lower than the experimental value of 40%. The discrepancy can be due to underestimation of the value of $k_{fP1}$ in the quantum chemical calculations. Another possible reason for this discrepancy can be underestimation of the reactor’s temperature. The temperature measurement in the reactor is a complex problem and a substantial uncertainty of this value can be expected. The rate constant sharply depends on temperature and this uncertainty can result in incorrect interpretation of the experimental result. For example, at the temperature $T = 1600 \text{ K}$, $k_{fP1} = 8.45 \times 10^3 \text{ s}^{-1}$ and Eq. (14) gives 43% for the efficiency of the 2-C$_{10}$H$_7$Br pyrolysis. This is in excellent agreement with the CFD calculations (46%). This estimation is closer to the experimentally measured efficiency of 40%, which forces us to assume that the real temperature of the reactor was closer to 1600 K.

5. Conclusions

Summarizing, we can conclude that the high-temperature micro-reactor can be used to measure kinetic constants of processes that last more than a few tens of microseconds. The results of CFD simulations testified (Fig. 5, dashed curve) that temperature distribution over most of the reactor interval between the electrodes can be nearly uniform for tubes with low values of thermal conductivity coefficients $\lambda \leq 2 \text{ W m}^{-1} \text{ K}^{-1}$. In this case, isothermal approximation can be applied for the interpretation of experimental data. By neglecting the
pressure, temperature, and component concentrations gradients across the flow, assuming a parabolic velocity profile throughout the reactor length, taking the centerline gas velocity at the outlet of the reactor to be equal to sonic, and neglecting slip of the gas velocity at the surface of the reactor, the analytical equations for the residence time (Eq. (9)), the number of collisions (Eq. (11)), relative fractions of components of interest at the reactor exit (Eq. (14) for bimolecular reactions and Eq. (15) for unimolecular reactions) have been derived. The calculated values of the efficiency of the 2-C_{10}H_{7}Br pyrolysis using Eq. (15) and CFD simulations are in satisfactory agreement. Even better agreement has been obtained between the calculated and experimental values of the inlet pressure $P_{in}$ as illustrated on Figs. 7 and 8. This confirmed that the assumptions taken are judiciously chosen.

At a low He flow rate, the free path becomes comparable with the tube radius and a flow slip occurs at the boundaries near the downstream end of the tube. This effect was taken into account in CFD simulations but was neglected when analytical expressions were deduced. CFD calculations reveal that there is a significant increase of slip velocity up to about 400 m/s closer to the exit of the tube. If this effect becomes significant only in a short interval, then it can be neglected, especially at elevated gas flow rates.

As follows from Fig. 8, the residence time shortens with a gas flow rate. At that, the residence time drops rapidly with the flow rate up to about 100 sccm and then decreases moderately. High values of $\tau_{res}$ at low gas flow rates are due to large pressure losses via friction. Therefore, measurements of kinetics constants of fast processes should be preferably carried out at elevated gas flow rates above 100 sccm. With such flow rates, a pulsed gas supply mode is worthy of consideration.

Eqs. (14) and (15) make it possible to easily interpret the experimental data and extract the values of the rate coefficients for (pseudo-)first-order ($n_B >> n_A$) bimolecular and unimolecular reactions, respectively. For example, a linear fit of an experimental plot of $ln \eta_A(y_2)/\eta_A(y_1)$ vs. $\eta_B$ at a fixed gas temperature and $\eta_A \ll \eta_B \ll 1$ allows one to determine the rate coefficient, as follows from Eq. (14). The rate coefficient for a unimolecular process can be then extracted from experimental dependences of $ln \eta_A(y_2)/\eta_A(y_1)$ on the reactor length $L$ or the total gas flow rate $g$ using Eq. (15). The more uniform the temperature distribution in the reaction zone, the higher the accuracy of the measurement. Thus, the micro-reactor can be employed for direct measurements of reaction rate constants, especially when secondary reactions are too slow to affect the consumption and production of the component of interest.
Acknowledgments

This work was supported by the Ministry of Education and Science of the Russian Federation under the Grant No. 14.Y26.31.0020 to Samara University. RIK acknowledges support from the U.S. Department of Energy, Basic Energy Sciences DE-FG02-03ER15411 for the calibration studies and the pyrolysis experiments.
References


Table 1. Experimental conditions for the measurements of pyrolysis of 2-C_{10}H_{7}Br.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>He flow rate</td>
<td>60 µmol/s</td>
</tr>
<tr>
<td>C_{10}H_{7}Br flow rate</td>
<td>5.4 nmol/s</td>
</tr>
<tr>
<td>Initial gas temperature</td>
<td>300 K</td>
</tr>
<tr>
<td>Output bulk pressure</td>
<td>10^{-6} Torr</td>
</tr>
<tr>
<td>SiC temperature(^a)</td>
<td>1500 K</td>
</tr>
</tbody>
</table>

\(^a\)At the center between molybdenum electrodes.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Pressure, Torr</th>
<th>Rate constant</th>
<th>Units</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{10}H_{7}Br → C_{10}H_{7} + Br</td>
<td>P1 = 7.5</td>
<td>k_{P1} = 0.31163 × 10^{24}/T^{2.4640} \exp(-42009/T) - 0.15229 × 10^{99}/T^{22.363} \exp(-84077/T)</td>
<td>s^{-1}</td>
<td>This work</td>
</tr>
<tr>
<td>P2 = 75</td>
<td>k_{P2} = 0.21831 × 10^{96}/T^{22.339} \exp(-73308/T) + 0.27782 × 10^{45}/T^{8.8080} \exp(-46476/T)</td>
<td>s^{-1}</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>7.5 ≤ P5 ≤ 75</td>
<td>k_{P1} + (k_{P2} - k_{P1}) × (\log(P1) - \log(P))/((\log(P1) - \log(P2))</td>
<td>s^{-1}</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>C_{10}H_{7} + Br → C_{10}H_{7}Br</td>
<td>7.5 ≤ P5 ≤ 75</td>
<td>0.92836 × 10^{17}/T^{5.8220} \exp(-9687.1/T) + 58.130/T^{3.7889} \exp(-1896.5/T)</td>
<td>cm^{3} s^{-1}</td>
<td>This work</td>
</tr>
<tr>
<td>Br_{2} → Br + Br</td>
<td></td>
<td>6.18 × 10^{-33} × (T/298)^{0.5} \exp(-134000/8.31/T)</td>
<td>s^{-1}</td>
<td>19</td>
</tr>
<tr>
<td>Br + Br + He → Br_{2} + He</td>
<td></td>
<td>3.2 × 10^{-33} × (298/T)^{1.26}</td>
<td>cm^{6} s^{-1}</td>
<td>20</td>
</tr>
</tbody>
</table>
Table 3. Viscosity coefficients and heat capacity ratios depending on the gas temperature.\(^{23}\)

<table>
<thead>
<tr>
<th>gas</th>
<th>Viscosity, (\mu) (g cm(^{-1}) s(^{-1}))</th>
<th>Heat capacity ratio, (\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>(2 \times 10^{-4} (T/300)^{0.5})</td>
<td>1.667</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>(10^{-4} (T/300)^{0.5})</td>
<td>(1.068 + 0.49\exp(-T/300.285))</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>(2 \times 10^{-4} (T/300)^{0.5})</td>
<td>(1.166 + 0.303\exp(-T/337.26))</td>
</tr>
</tbody>
</table>
Figure captions

Figure 1. Sketch of the micro-reactor: 1 - SiC tube, 2 - molybdenum electrodes, 3 - alumina holder, 4 - copper heat exchanger, 5 - graphite slivers.

Figure 2. The gas scheme for measuring the pressure drop in the tube of the SiC chemical reactor. PC is a personal computer; $V_i$ denote valves, $P_{in}$ and $P_{ex}$ are pressure gauges located in the gas duct upstream and downstream of the tube respectively; MFC is a Mass-Flow Controller.

Figure 3. Total energy corrections for 1-bromonaphthalene ($\Delta E_{\text{total}} = \Delta E_{\text{geom}} + \Delta E_{\text{Method}}$) calculated using two-point CBS extrapolations: black – with the cc-pVTZ and cc-pVDZ basis sets, red – with the cc-pVTZ and cc-pVQZ basis sets.

Figure 4. Calculated rate constants for dissociation of 1- (a) and 2-bromonaphthalene (b) at different pressures. Black squares – 0.01 atm, red circles – 0.0395 atm, blue triangles – 0.1 atm, magenta down-pointing triangles – 0.3 atm, green diamonds – 1 atm, purple left-pointing triangles – high pressure limit.

Figure 5. CFD simulation of distributions of pressure $P$, temperature $T$, and axis velocity $U_0$ for the gas stream along the axis of the micro-reactor under the experimental conditions. The dashed line represents the temperature distribution for $\lambda = 2$ W m$^{-1}$ K$^{-1}$.

Figure 6. CFD calculation of the 1-C$_{10}$H$_7$Br pyrolysis efficiency along the axis of the micro-reactor for temperatures $T = 1500$ (solid curve) and 1600 K (dashed curve) at the point of the reactor’s wall between the electrodes.

Figure 7. Inlet pressure dependences versus the CO$_2$ flow rate at ambient temperature measured experimentally (■) and calculated with Eq. (6) (●) and CFD simulations (▲).

Figure 8. Inlet pressure dependences versus the He flow rate at ambient temperature measured experimentally (■) and calculated with Eq. (6) (●) and CFD simulations (▲).
**Figure 9.** Calculated pressure distributions along the flow at $T = 1500$ K and $g = 400$ sccm for two carrier gases, C$_2$H$_4$ and He.

**Figure 10.** Residence time as a function of the gas flow rate for $L = 1$ cm and the gas temperature of 1000 K for He, C$_2$H$_4$, and CO$_2$. 
Figure 2
Figure 3
Figure 4
Figure 6
Figure 7
Figure 8
Figure 9

[Graph showing pressure $P(z)$ vs. length $z$ with labels for $C_2H_4$ and He, and curves for Eq. 6, Eq. 5, and CFD.]
Figure 10.