# OVERALL KINETICS OF ISOBUTANE CATALYTIC COMBUSTION ON A PLATINUM WIRE AT HIGH TEMPERATURES

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Overall reaction orders and activation energies for catalytic combustion of stoichiometric i-butane/air mixtures on a platinum wire within the temperature range 660 and 1003 K, for total pressures between 10 and 70 kPa were determined and reported. The measurements were carried out using the technique of isothermally heated platinum wire, able to monitor the chemical heat flow rate, related to the rate of the catalytic reaction. The experimental results were rationalized using both the transient and stationary regimes, described by a three parameter equation. The obtained kinetic parameters were discussed in terms of the elementary steps of the overall combustion process. The negative activation energy found at higher temperatures was attributed to reactant depletion within the diffusion layer.

## INTRODUCTION

Combustion of alkanes, with its newest variant – catalytic combustion – is one of the most important sources of energy. The increasing attention paid to catalytic combustion arises from the legitimate concern regarding the pollutant abatement, a subject approached by a continuously augmented scientific community. Recent analysis of the present status of knowledge concerning the kinetics of catalytic combustion evidenced the role of the fuel nature, indicating a significant decrease of the activation energy when the hydrocarbon chain increases, but the effect of branching seems to be still unclear.[1] The few available overall activation parameters for *i*-butane catalytic combustion on platinum surface are not in very good agreement[1-4] and the differences could be assigned to experimental conditions (composition, temperature, presence of inert compounds) as well as to the theoretical approach. On the other hand, *i*-butane is an important component as a feedstock in petrochemical industry and in the nowadays combustion systems due to its increased use as a component of the liquefied petroleum gas (LPG), as well as a safer agent for refrigeration systems. Many of its properties are similar to those of *n*-butane, but branching is expected to bring in

significant mechanistic differences regarding the catalytic combustion. The kinetic studies on the catalytic combustion of *i*-butane were carried out especially within a temperature range beginning with the characteristic catalytic ignition temperature and extending more or less to kinetic control range, where the activation energy is generally high, connected with the catalytic activation of C-H bond, considered as the rate limiting step.[1] At higher temperatures, of increased interest for the design of short residence time catalytic reactors, the activation energy decreases continuously until the whole process becomes diffusion controlled. Moreover, a further temperature increase can result in a depletion of reactants within the layer adjacent to catalyst surface, which cannot be compensated anymore by diffusion. The overall result is a decrease of the reaction rate when the temperature increases, a behavior formally associated with negative activation energy (anti-Arrhenius kinetics).[5] Such a phenomenon can be easily identified using the technique of an isothermally heated platinum wire, which offers the possibility to measure the reaction rate of the catalytic process within a wide temperature range. This technique allows determination of the catalytic reaction rate as a function of composition (including the presence of different additives), total gas pressure and catalyst temperature. From the

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analysis of these data, according to a kinetic model, the characteristic kinetic parameters can be evaluated.[6] This procedure is applied in the present paper to obtain the kinetic parameters for the catalytic combustion of stoichiometric *i*-butane/air mixtures on platinum wire at total pressure between 10 and 70 kPa and high temperatures (660 – 1003 K).

## EXPERIMENTAL METHOD

The experiments were carried out with an equipment described in detail elsewhere.[6,7] Briefly, the fuel/air mixture or the air is introduced into the evacuated test cell at identical initial pressures. A platinum wire located in the centre of the cell is heated according to a quasi-rectangular profile and maintained at constant temperature. The exothermal reaction occurring on the surface of the platinum wire delivers a supplementary quantity of heat which is compensated by a decrease of the input power in order to maintain a constant temperature. This can be measured and compared to the similar quantity when the test cell contains only air. The measured quantity during both transient and stationary regime is the voltage drop, $U_{std}$, across a standard resistor connected in series with the platinum wire. The chemical heat flow rate $F_r = dQ_r/dt$ can be calculated as:[7]

$$dQ_r/dt = (R_w/R_{std}^2) \cdot \left[ (U_{std}^2)_{air} - (U_{std}^2)_{mixture} \right] \quad (1)$$

where $R_w$ and $R_{std}$ are the resistances of the platinum wire and of the standard resistor, respectively. The mixture of known composition is prepared by the partial pressure measurement and the temperature is calculated from the wire resistance measurements according to literature recommendation:[8]

$$T_w = 273.15 + D_0 + \sum_{i=1}^{9} D_i \cdot \left[ \frac{x - 2.64}{1.64} \right]^i \quad (2)$$

where $D_0$, $D_j$ are constants given in literature and $x$ is the ratio between the wire resistance at temperature $T_w$ and at 273.15 K.

## RESULTS AND DISCUSSION

A typical experimental result is illustrated in Fig. 1 for a stoichiometric *i*-butane/air mixture diluted with argon in ratio 1:3, at a total gas pressure $p_0 = 60$ kPa and for platinum wire temperature $T_w = 703$ K. It was previously shown that the resulted $F_r$ vs. time curve can be modeled taking into account the contribution of diffusion and of surface reaction to the overall catalytic combustion process obtaining the following equation:[6]

$$F_r = a + b \cdot (1 - \exp(-ct)) \quad (3)$$

where $a$ is a constant dependent on the heat delivered in the immediate vicinity of the wire at the beginning of the ignition process, $b = \dfrac{\Delta^c H_T^0 \cdot S \cdot k_D \cdot k_r \cdot C_0}{k_D + k_r}$ and $c = (k_D + k_r)/\phi$, with $\Delta^c H_T^0$ – the standard heat of combustion at temperature $T$, $S$ – the surface of the platinum wire, $C_0$ – the molar concentration of fuel in the mixture, $k_r$ and $k_D$ – the rate constants for surface reaction and diffusion, respectively and $\phi$ – a characteristic length which can be taken equal to unity, introduced to obtain a physically correct dimension for the parameter $c$.
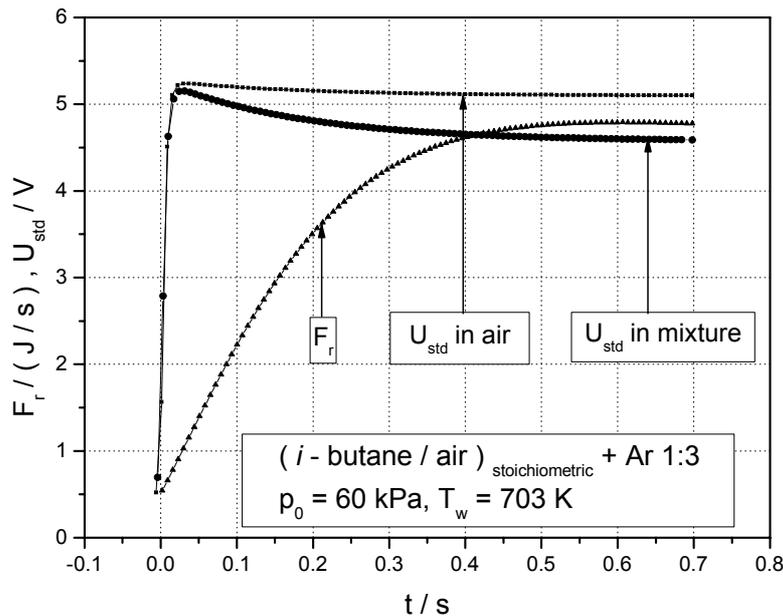


Fig. 1 – Primary $U_{std}$ vs. time data in air and in mixture and calculated $F_r$ vs. time curve.

The transient period of the combustion, represented by the increasing part of $F_r$ vs. time curve, is followed by a stationary period, represented by the horizontal part, when $\exp(-ct) \to 0$. It can be seen that for a diffusion control, when $k_r \gg k_D$, the parameters $b$ and $c$ get simpler meanings:

$$b = \Delta^c H_T^0 \cdot S \cdot k_D \cdot C_0 \quad c = k_r / \phi \qquad (4)$$

On the other hand, the reaction rate of the catalytic process, $r_s$, measured through:

$$r_s = \frac{1}{\Delta^c H_T^0 \cdot S} \cdot F_r \qquad (5)$$

can be rationalized as an empirical, Arrhenius type, equation:

$$r_s = = A_0 \cdot (p_0 / p^*)^n \cdot e^{-E_a / RT_w} \qquad (6)$$

with $A_0$ the pre-exponential factor, $p^*$ the standard pressure (taken as $p^* = 101.3$ kPa), $n$ the overall reaction order and $E_a$ the overall activation energy. A more elaborate approach is a mechanistic Langmuir-Hinshelwood equation for a competitive, nondissociative adsorption of both reactants, without diffusion limitation:[3]

$$r_s = k_s \cdot \frac{K_F \cdot K_{ox} \cdot p_F \cdot p_{ox}}{(1 + K_F \cdot p_F + K_{ox} \cdot p_{ox})^2} \qquad (7)$$

where $p_F$ and $p_{ox}$ are the partial pressures of fuel and oxygen, respectively, $K_F$ and $K_{ox}$ the corresponding adsorption-desorption equilibrium constants and $k_s$ is the rate constant of the surface reaction.

The regression of stationary values of $F_r$ at constant temperature for different total pressures and at constant pressure for different temperatures allows the evaluation of the overall reaction orders and activation energies, according to equation (6). A typical result for the reaction order is illustrated in Fig. 2.

The obtained reaction order, $n = 0.25$, indicates a significant increase of the reaction rate with the total pressure.

The overall activation energies, evaluated from the regression of $F_r$ against $1/T_w$, given in Table 1 for a temperature range between 650 and 860 K, are typical for diffusion control in the gas phase.
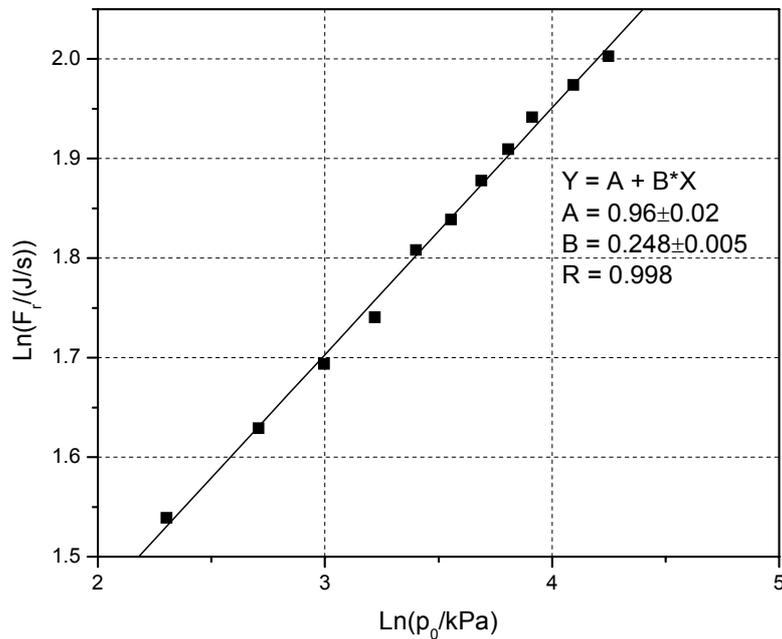


Y = A + B*X
A = 0.96±0.02
B = 0.248±0.005
R = 0.998

Fig. 2 – Evaluation of the reaction order from stationary values of $F_r$ for the stoichiometric
$i$-butane/air mixture at $T_w = 690$ K.

*Table 1*

Activation energies for the catalytic combustion of a stoichiometric $i$-butane/air mixture, evaluated using equations (5) and (6) from stationary values of $F_r$

| $p_0$/kPa | 10 | 30 | 50 | 70 |
|---|---|---|---|---|
| $E_a$/(kJ/mol) | 5.4 ± 0.3 | 7.9 ± 0.4 | 10.3 ± 0.6 | 8.0 ± 0.5 |

The transient period allows the evaluation of parameters *a*, *b* and *c* from equation (3) for different total pressures and temperatures using a nonlinear regression analysis. The temperature dependence of parameters *b* and *c* gives the activation energies for diffusion and surface reaction, assuming that the overall process is diffusion controlled, according to equations (4). A typical result for the surface reaction is given in Fig. 3 at $p_0 = 70$ kPa. The corresponding activation energy is significantly larger than the characteristic diffusion value, but lower than the value reported in literature at ignition temperature. Similar values were also obtained at other pressures.

The temperature dependence of parameter *b* is different for lower and higher temperature ranges. At lower temperatures the regression $\ln(b)$ against $1/T_w$ is of Arrhenius type, resulting in small activation energies, characteristic to diffusion controlled processes, as illustrated in Fig. 4.
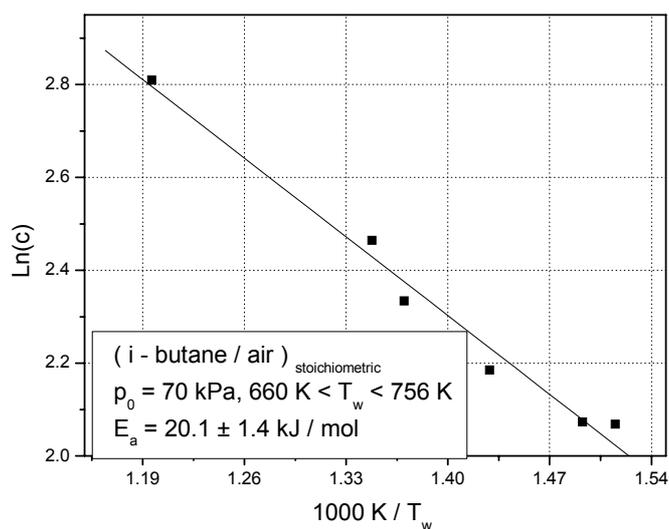


Fig. 3 – Arrhenius plot of parameter *c*, characteristic to surface reaction.
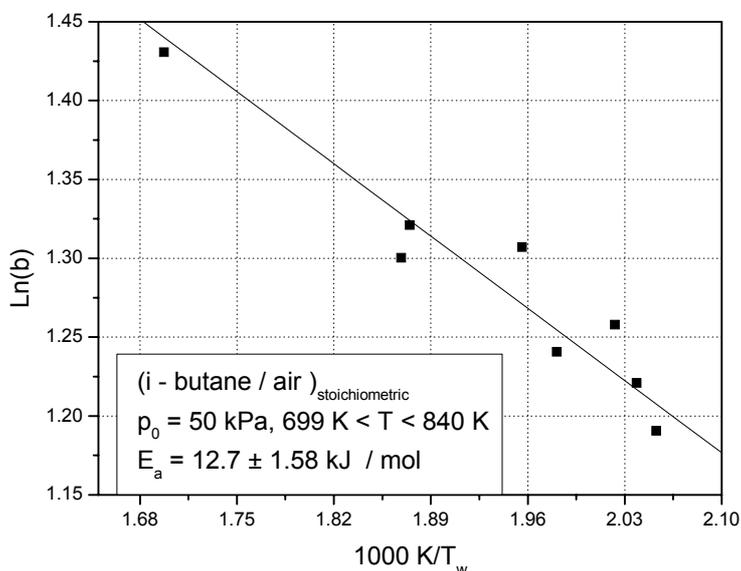


Fig. 4 – Arrhenius plot of parameter *b*, characteristic to diffusion, at lower temperatures.

Similar values were also obtained at other total pressures within the same temperature range. At higher temperature the dependence is reversed, indicating a decrease of the diffusion rate with the temperature increase. The phenomenon was predicted theoretically[5] and was also confirmed for *n*-butane/air mixtures using the same technique of isothermally heated platinum wire.[6] It is attributed to reactant depletion within the diffusion layer and is induced by both high temperatures and catalytic surface. The overall effect is a decrease of the reaction rate, a phenomenon which becomes important in reactors with short residence times, when a supplementary increase of temperature has an adverse effect than anticipated. A typical result

is illustrated in Fig. 5. Similar results were also obtained for other pressures.

A quantitative explanation of this pattern was originally advanced on the basis of a detailed analysis of all component steps.[5] A simpler but more accessible semi-quantitative formulation was used to explain the similar behavior for *n*-butane.[6] The results can be also analyzed and discussed using the mechanistic Langmuir-Hinshelwood equation (7). Earlier discussions reported in literature in connection with this equation assumed that $K_{ox} \cdot p_{ox} \gg 1 + K_F \cdot p_F$ due to the stronger

adsorption of oxygen, implying that the reaction rate is independent on the total pressure.[3,4] On the other hand, at very low total pressures it can be supposed that $K_F \cdot p_F + K_{ox} \cdot p_F \ll 1$, implying that the reaction rate is directly proportional with $p_0^2$.[6] Neither the first assumption nor the second one can be verified using the present data. Only the dependence $1/F_r$ versus $1/p_0$ shows a very good correlation, indicating a more complex mechanism.
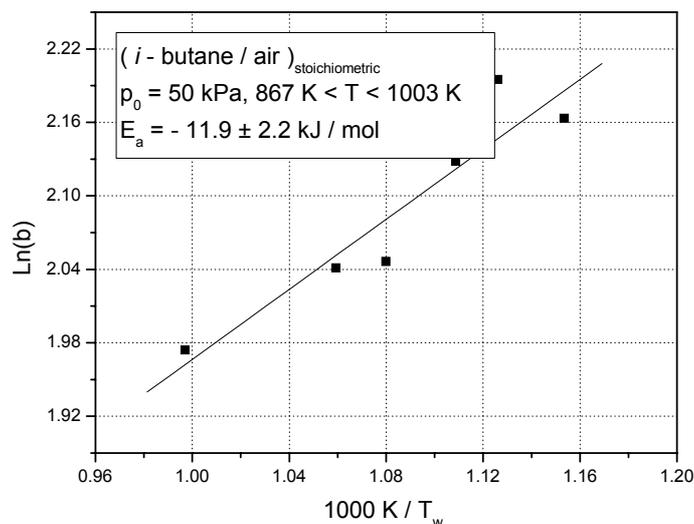


Fig. 5 – Anti-Arrhenius behavior of parameter *b* for catalytic combustion of the stoichiometric *i*-butane/air mixture at high temperatures.

## CONCLUSIONS

The measurement of the chemical heat flow rate using the technique of isothermally heated platinum wire allowed the determination of the overall reaction orders and activation energies for the catalytic combustion of a stoichiometric *i*-butane/air mixture. The measurements were performed within the pressure range $10 \div 70$ kPa and temperature range $660 \div 1003$ K. The overall reaction order (with respect to total pressure) was $n \approx 0.25$, indicating a significant increase of the reaction rate with respect to the total pressure. At lower temperatures (below 800 K) the activation energy for the diffusion step is positive and has low values, characteristic for this process ($\leq 12$ kJ/mol). At higher temperatures, between 850 and 1000 K, the activation energy of diffusion becomes negative, a result attributed to the reactant depletion within the diffusion layer, when the very fast consumption of the reactants cannot

be compensated anymore through molecular diffusion. The activation energy of the surface reaction is significantly larger (around 20 kJ/mol) suggesting that a further temperature increase would lead to an increase of the surface reaction rate. The overall process is actually limited by the diffusion step. The general kinetic characteristics of *i*-butane catalytic combustion on platinum within the specified ranges of experimental conditions are similar with those reported for *n*-butane.

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