KINETICS OF ISOTHERMAL IGNITION OF PROPANE/AIR MIXTURES ON PLATINUM

Dumitru OANCEA,[a*] Octavian STAICU[a,b] and Valentin MUNTEANU[a]

[a]Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, 4-12 Bd. Elisabeta, 030018 Bucharest, Roumania
[b]"Ilie Murgulescu" Institute of Physical Chemistry, Roumanian Academy, 202 Spl. Independentei, 060021 Bucharest, Roumania

The overall kinetics of catalytic combustion of stoichiometric propane/air mixture on isothermally heated platinum wire was investigated at various temperatures and total pressures. The induction periods and the diffusion controlled reaction rates were measured using a thin platinum wire immersed in a fuel/air mixture and heated according to a quasi-rectangular temperature profile. The changes of the required input power induced by the exothermal catalytic reaction were recorded and utilized to extract the necessary information for the kinetic analysis. The overall kinetic parameters were evaluated and discussed.

INTRODUCTION

The heterogeneous catalytic combustion of alkane/air mixtures, a promising alternative for a cleaner conversion of chemical energy stored in hydrocarbons into thermal, electrical or mechanical energy, has known an increased interest during recent years. The catalytic ignition represents an important step of the overall process, playing a key role in understanding and adjusting the safe and optimal operation of practical combustion devices. Depending on the operational parameters such as fuel, mixture composition, gas pressure and movement, catalyst nature and configuration, the ignition occurs at characteristic temperatures which indicate a rapid change of the reaction rate from low to high values, often associated with a sudden transition of the overall process from kinetic to mass transfer control.[1] However, the pressure dependence of the heterogeneous combustion reaction rate[2, 3] as well as the high activation energies[4, 5] frequently reported in literature within the range of significant conversion rates, when the surface reaction is already 'ignited', suggest the existence of a progressive transition implying a significant mixed control.[6] The

most reliable published data regarding the ignition temperatures have been obtained at normal pressure using the stagnation point flow[7-9] based on the temperature recording of an electrically heated noble metal foil catalyst against the input power as the controlled variable. The extinction temperatures thus measured are higher than the associated ignition temperatures due to the exothermal combustion reactions occurring on the catalyst surface and resulting in an increase of its temperature. When the controlled variable is the catalyst temperature and the response variable is the reaction rate or a quantity proportional to it, the hysteresis loop may look different, with inverted order of ignition and extinction temperatures.[10, 11] The ignition temperatures of various fuel/air mixtures have also been measured using the heated wire technique.[12-14] Moreover, the use of a thin platinum wire heated in an isothermal regime according to a quasi-rectangular temperature profile in stagnant fuel/air mixtures[15] allows the measurement of the ignition and extinction temperatures at various total pressures broadening the area of the controllable parameters.[14] The ignition temperature dependence on the mixture composition and pressure allows

* Corresponding author: doan@gw-chimie.math.unibuc.ro

the evaluation of the relevant parameters for the kinetics of catalytic combustion.[14, 16-18] On the other hand, the method using an isothermally heated platinum wire allows for the measurement of the induction period as long as it is significantly longer than the rise time of the quasi-rectangular temperature profile (1 to 2 ms). In turn, the analysis of the temperature and total pressure dependence of the induction period suggests an alternative method for the evaluation of the overall kinetic parameters.

EXPERIMENTAL

The experimental measurements were carried out using the equipment and procedure described in details previously[6, 14, 15] and given schematically in Fig. 1.
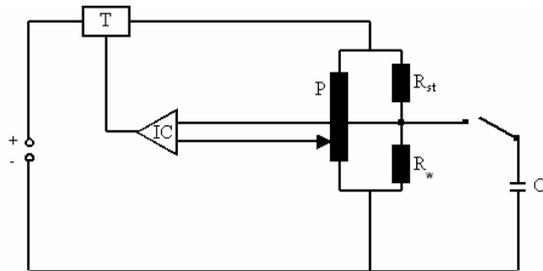

Fig. 1 – Schematic representation of the electrical circuit able to heat the platinum wire according to a quasi-rectangular profile.

A platinum wire of 0.1 mm diameter and 45 mm length (99.99% from Aldrich), connected through brass conductors in a heating circuit, is immersed in the center of a cylindrical test cell of 9 cm diameter and height, containing either air or fuel/air mixture at a prescribed pressure. It is heated according to a quasi-rectangular profile, with a rise time of $1 - 2$ ms using the discharge of a capacitor C followed by a controlled feeding system designed to maintain a constant wire temperature. A standard resistor R_{std}, connected in series with the wire of resistance R_w, forms a Wheatstone bridge with the potentiometer P and allows the measurement of the input power, recording the variation of the voltage drop U_{std} during the test. Any unbalance of the bridge is detected by the integrated circuit IC which readjusts the voltage applied across R_w through the series transistor T in order to maintain its resistance constant. The diagram U_{std} versus time contains the information necessary for the kinetic study. To evaluate the heat flow rate dQ_r/dt due to the catalytic reaction occurring on the wire it is necessary to eliminate the power dissipated through the heat transfer from the hot wire to the surroundings. The wire temperature is calculated from its resistance using a calibration procedure.[15] The fuel/air mixture of known composition (4.02% propane) was obtained by the partial pressures method in storage tanks at 4 bar and used after 24 h.

RESULTS

The kinetically relevant quantity dQ_r/dt, representing the heat flow rate associated with the surface chemical reaction, can be obtained from the experimental diagrams recorded in air and in a fuel/air mixture in similar conditions as:

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

where R_w and R_{std} are the resistances of the platinum wire and of a standard resistor connected in series with the wire, respectively, and U_{std} is the voltage across the standard resistor during the isothermal heating.
It is related to the catalytic reaction rate through:

$$r_s = dQ_r/dt \big/ (\Delta^c H_T^0 \cdot S) \tag{2}$$

where $\Delta^c H_T^0$ is the standard heat of combustion at the working temperature and S is the surface of the platinum wire. A typical pair of U_{std} versus time diagrams is given in Fig. 2.

The diagram recorded in mixture presents three distinct zones: an induction period (or induction delay), τ_i, where the difference between air and fuel/air diagrams is very small and the combustion reaction is kinetically controlled, a transient period characterizing the ignition process, and a quasi-steady state combustion where the reacted fuel is replenished through diffusion and natural convection. The last zone remains approximately constant until the bulk fuel concentration decreases significantly. Here the reaction heat flow rate dQ_r/dt of the catalytic combustion reaches its maximum values and is under the mass transfer or mixed control.[6]
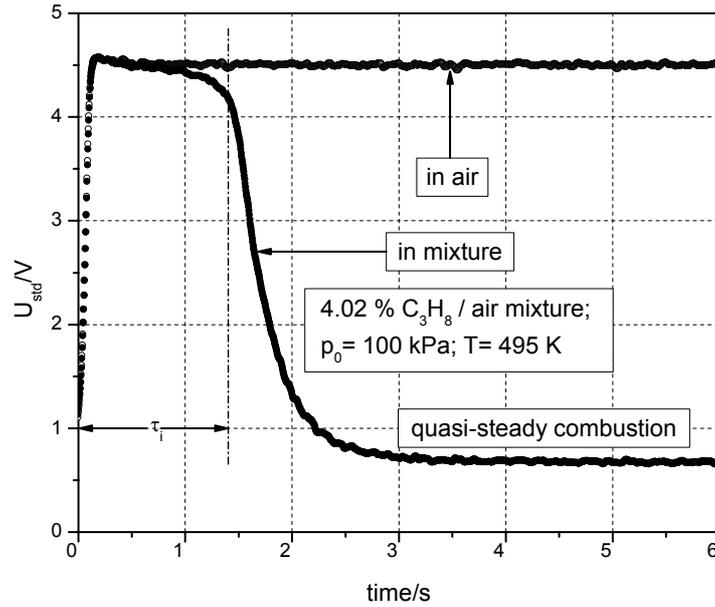
Fig. 2 – Experimental U_{std} versus time diagrams.

DISCUSSION

Pressure dependence of the overall reaction rate after ignition

The variation of the reaction heat flow rate, calculated according to (1), is illustrated in Fig. 3 for the stoichiometric propane/air mixture. The results can be analyzed using an empirical Arrhenius-type rate law:

$$dQ_r / dt = A_0 \cdot (p_0 / p^*)^n \cdot e^{-E_a / RT_w} = a_0 \cdot p_0^{b_0} \tag{3}$$

where A_0 is proportional to the preexponential factor, p_0 the total gas pressure, p^* the standard pressure (taken as $p^* = 101.3$ kPa), n the overall reaction order, E_a the overall activation energy, R the universal gas constant, a_0 a constant and $b_0 = n$.
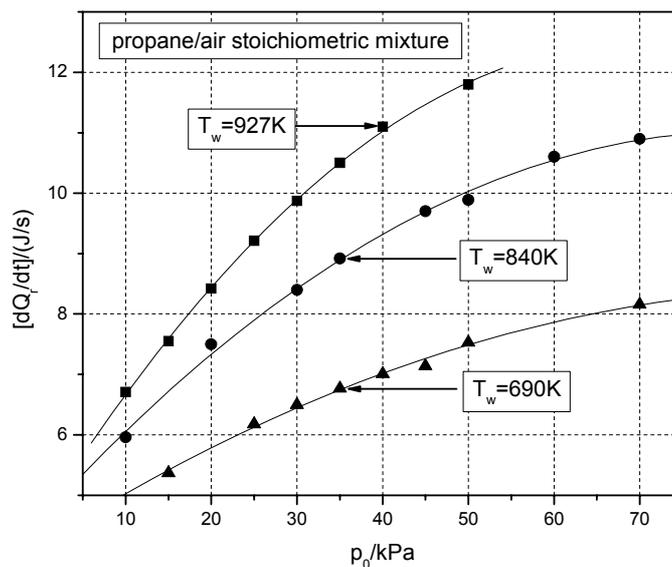

Fig. 3 – Typical reaction heat flow rate variation with the total pressure at different wire temperatures.

A more advanced treatment relies on a mechanistic Langmuir-Hinshelwood equation for a competitive, non-dissociative adsorption of both reactants without diffusion limitations:[3, 7]

$$dQ_r/dt = \frac{a_1 \cdot p_0^2}{(1 + b_1 \cdot p_0)^2} \qquad (4)$$

where a_1 and b_1 are constants. Other assumptions regarding the significant steps of the overall process lead to kinetic equations of different forms.[3] A mechanism based on a mixed (diffusion and heterogeneous reaction) control,[6] assuming that the reaction is first order with respect to fuel and m order with respect to O_2, leads to a kinetic equation of the form:

$$dQ_r/dt = \frac{a_2 \cdot p_0^{1+b_2}}{1 + c_2 \cdot p_0^{b_2}} \qquad (5)$$

where a_2, c_2 are constants and $b_2 = m$.

The results obtained by fitting Equations (3), (4) and (5) on the data shown in Fig. 3 for the stoichiometric propane/air mixture at $T_w = 840$ K are given in Table 1.

Table 1

Fitting parameters for Equations (3)-(5) on the reaction heat flow rates against total pressure for the stoichiometric propane/air mixture at $T_w = 840$ K

	Eq. (3)	Eq. (4)	Eq. (5)
r^2	0.997	0.956	0.998
a	2.98±0.07	0.50±0.08	3.69±0.48
b	0.31±0.01	0.20±0.02	–0.74±0.05
c	-	-	0.75±0.52

The coefficient of determination r^2 has comparable values for Equations (3) and (5) and is significantly higher than that for Equation (4). Additionally, the parameter b of Equation (5) has a meaningful significance in agreement with the established inhibitory effect of O_2 on the catalytic combustion of alkanes on platinum.[5] At the same time the overall reaction order calculated for a first order with respect to propane is 0.26, a figure close to that resulted from Equation (3). It seems that Equation (5), based on a mixed control of the combustion rate, is the most adequate to describe the pressure dependence of the catalytic reaction rate with respect to pressure.

Ignition period dependence on the wire temperature and gas pressure

According to a previous paper[14] the variation with the wire temperature and gas pressure of the induction period illustrated in Fig. 2 can be described by the following equation:

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

where β is a proportionality constant including the pre-exponential factor. The usefulness of this equation to explain the experimental results is illustrated for the stoichiometric propane/air mixture. The regression analysis of the pressure dependence of induction period for the catalytic ignition in isothermal conditions gives overall reaction orders similar to those reported above (*e. g.* $n = 0.28 \pm 0.06$ at $T_w = 549$ K). More challenging is the temperature dependence of the induction period which offers the possibility to evaluate the activation energy during the kinetic control. This can be compared with the corresponding activation energy of the quasi-steady combustion when the overall process is controlled by the mass transfer or occurs under a mixed control. The associated activation energy can be evaluated from the regression of $\ln(dQ_r/dt)$ versus $1/T_w$. The temperature dependence of the ignition period is illustrated in Fig. 4.

The result, $E_a = 100$ kJ/mol, agrees well with other reported values evaluated using different experimental techniques (97 kJ/mol[4], 92 kJ/mol[5], 80 kJ/mol[7]), validating the proposed method. In the same conditions the regression of $\ln(dQ_r/dt)$ versus $1/T_w$ gives $E_a = 11.5$ kJ/mol, a value characteristic for mixed or mass transfer control (Fig. 5).
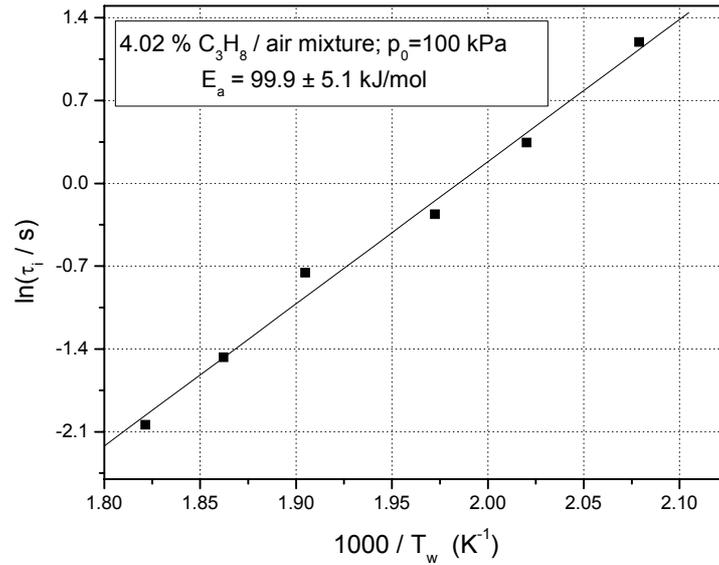
Fig. 4 – The variation of the ignition period with the wire temperature
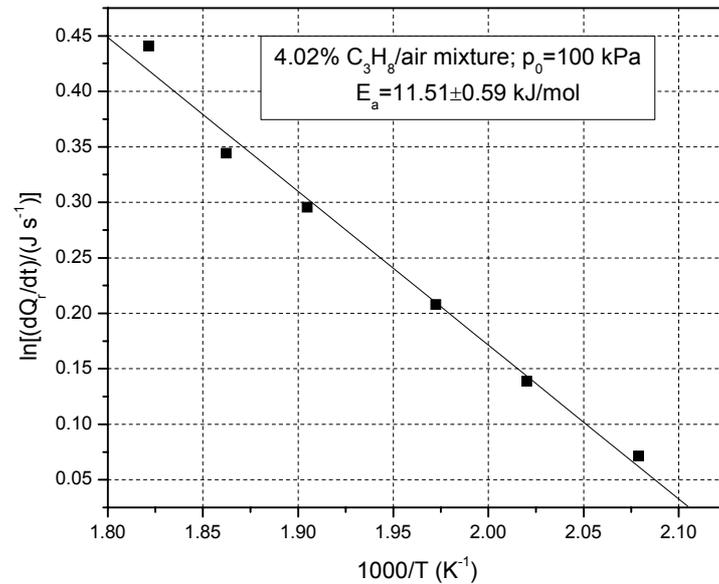for the stoichiometric propane/air mixture at $p_0 = 100$ kPa.

Fig. 5 – The temperature dependence of the reaction heat flow rate dQ_r/dt
for a stoichiometric propane/air mixture.

Table 2

Activation energies from induction period and from reaction heat flow rate
measurements at various pressures for the stoichiometric propane/air mixture

p_0/kPa	E_a (kJ/mol)	
	From τ_i	From dQ_r/dt
100	99.9 ± 5.1	11.5 ± 0.6
70	92.6 ± 8.0	10.9 ± 0.5
50	58.9 ± 4.6	13.6 ± 0.8
30	56.3 ± 5.7	11.5 ± 0.9

The activation energy for the kinetically controlled process decreases monotonically with pressure. This trend is in agreement with the predictions of the kinetic equation obtained on the basis of the Langmuir-Hinshelwood model for a competitive, non-dissociative adsorption. For mixed or mass transfer control the overall activation energy should remain low and practically constant. The results from a similar regression analysis at various pressures are given in Table 2.

CONCLUSIONS

The catalytic ignition of the stoichiometric propane/air mixtures using an isothermally heated platinum wire at various temperatures and at atmospheric and sub-atmospheric pressures was investigated measuring the ignition periods and the limiting (mass transport limited) reaction heat flow rates. The pressure dependence of the catalytic reaction rate after ignition, measured as the reaction heat flow rate, was determined and analyzed using several models. The results indicate that after ignition the overall process is mixed controlled. From the pressure and temperature dependence of the induction periods, the overall kinetic parameters were obtained in agreement with other ignition data.

REFERENCES

1. M. Rinnemo, O. Deutschmann, F. Behrendt and B. Kasemo, *Combust. Flame*, **1997**, *111*, 312-326.
2. J. Mantzaras, *Catal. Today*, **2006**, *117*, 394–406.
3. S. R. Deshmuch and D. G. Vlachos, *Combust. Flame*, **2007**, *149*, 366-383.
4. M. Aryafar and F. Zaera, *Catal. Lett.*, **1997**, *48*, 173-183.
5. Y.-F. Yu Yao, *Ind. Eng. Chem. Prod. Res. Dev.*, **1980**, *19*, 293-298.
6. O. Staicu, V. Munteanu, and D. Oancea, *Catal. Lett.*, **2009**, *129*, 124-129.
7. G. Veser and L.D. Schmidt, *AIChE J.*, **1996**, *42*, 1077-1087.
8. M. Ziauddin, G. Veser and L.D. Schmidt, *Catal. Lett.*, **1997**, *46*, 159-167.
9. W. R. Williams, M. T. Stenzel, X. Song and L. D. Schmidt, *Combust. Flame*, **1991**, *84*, 277-291.
10. L. Kiwi-Minsker, I. Yuranov, B. Siebenhaar and A. Renken, *Catal. Today*, **1999**, *54*, 39-46.
11. K. Arnby, J. Assiks, P. A. Carlsson, A. Palmqvist and M. Skoglundh, *J. Catal.*, **2005**, *233*, 176-185.
12. C. G. Rader and S. W. Weller, *AIChE J.*, **1974**, *20*, 515-522.
13. P. Cho and C.K. Law, *Combust. Flame*, **1986**, *66*, 159-170.
14. O. Staicu, D. Razus, V. Munteanu and D. Oancea, *Centr. Eur. J. Chem.*, **2009**, *7*, 478-485.
15. D. Oancea, O. Staicu, V. Munteanu, and D. Razus, *Catal. Lett.*, **2008**, *121*, 247-254.
16. T. Perger, T. Kovács, T. Turányi and C. Treviño, *J. Phys. Chem.*, **2003**, *B 107*, 2262-2274.
17. L. Hiam, H. Wise and S. Chaikin, *J. Catal.* **1968**, *9-10*, 272-276.
18. A. Schwartz, L. L. Holbrook and H. Wise, *J. Catal.* **1971**, *21*, 199-207.