Ignition on Catalytic Wires: Kinetic Parameter Determination by the Heated-Gas Technique

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The analysis of ignition phenomena occurring during catalytic oxidation over electrically-heated wires has been recently discussed (Rader and Weller, 1974). This paper also contained (first-order) kinetic parameters deduced for the oxidation of butane over electrically-heated platinum.

The present note contains new data for the ignition of butane-oxygen mixtures over platinum, obtained by a different experimental method: the heated-gas technique introduced by Cardoso and Luss (1969). A new rectifying plot is developed for the extraction of Arrhenius parameters from such heated-gas ignition data. This analysis, applied to our own experimental data, gives values for the kinetic parameters that are reasonably consistent both with the parameters deduced by us from ignition data given by Cardoso and Luss (1969) and also with the parameters previously derived from data with the electrically-heated wire technique (Rader and Weller, 1974).

THEORY

The Frank-Kamenetskii (1941) theory of thermal ignition has been the starting point for all analyses to date. The heated-gas technique of Cardoso and Luss (1969) has the theoretical advantages of (1) not requiring an I^2R term in the heat balance and (2) permitting valid use of Frank-Kamenetskii's approximate expansion for the Arrhenius rate constant, and the practical advantage of largely eliminating the axial temperature gradient in the catalytic wire that is inherent in the heated-wire technique. It has the disadvantage that the convenient rectifying plot developed by Hiam et al. (1968) cannot be used for determination of the kinetic parameters because the quantity $(T_w^* - T_0)$ required for this purpose is very small at ignition (with the heated-gas technique) and is not easily measured with the required degree of accuracy. An alternate rectifying plot can be developed.

The steady state heat balance equation for first-order kinetics is

$$\frac{(-\Delta H)C_0}{1/k(T_w) + 1/\beta} = \alpha(T_w - T_0) \qquad (1)$$

The Frank-Kamenetskii tangency condition for ignition requires that at the ignition temperature T_w^* the heat removal line be tangent to the heat generation curve. Frank-Kamenetskii (1941) showed that at ignition the following equation is satisfied:

$$\beta/k(T_w^*) = \xi \qquad (2)$$

where

$$\xi \equiv \frac{(-\Delta H)EC_0\beta}{\alpha R T_0^2} \qquad (2A)$$

Although this fact is not explicitly presented in the original work of Frank-Kamenetskii, Equation (2) may be transformed into the equivalent logarithmic form:

$$\ln\left(\frac{C_0}{T_0^2}\right) = \frac{E}{R}(1/T_w^*) + \ln\left(\frac{\alpha R}{Z(-\Delta H)E}\right) \qquad (3)$$

Equation (3) permits a rectifying plot of $\ln(C_0/T_0^2)$ against $1/T_w^*$ to be made from experiments in which, at constant flow rate, T_w^* is measured as a function of C_0 and T_0. The Arrhenius activation energy E is determined from the slope; the pre-exponential Z may be determined from the intercept provided that the heat transfer coefficient α is independently measured.

The heat transfer coefficient can be determined by electrically heating the wire in a flowing, nonreactive (O_2) gas stream (Rader and Weller, 1974). The mass transfer coefficient β is then determined from measurements in the upper thermal regime where mass transfer is rate-limiting.

EXPERIMENT

Apparatus

The apparatus was similar to that used by Rader and Weller (1974). The catalytic filament, supported by insulated stainless steel rods, was mounted horizontally in a 4.13-cm diameter reactor. The filament was connected in series with a 10,000-ohm resistor and a current-regulated d.c. power supply; a constant current of 1.0 ma was maintained through the filament circuit. The gas temperature was monitored by an iron-constantan thermocouple positioned 0.3 cm downstream of the catalytic filament. External heating of the reactor and preheat zone was by a Marshall tube furnace controlled by a Hewlett-Packard 240M temperature programmer.

The reactant gas mixture was prepared by metering oxygen (predried through Davison 4A zeolite) and *n*-butane (99.995+% purity) separately through calibrated rotameters, to a mixing and preheating chamber containing stainless steel baskets. The mixed stream then passed axially through the reactor normal to the catalytic filament. Platinum wire of 99.99+% purity, purchased from United Mineral and Chemical Corporation, was used as catalyst.

Procedure

The activation procedure was identical to that described by Rader and Weller (1974). This involved electrical heating of the platinum filament to approximately 800°C in a 1% butane-99% oxygen mixture for 25 min. prior to each experiment.

Application of Equation (3), the heated-gas rectifying equation for a first-order, irreversible reaction, requires knowledge of T_w^* as a function of C_0. For this purpose, in any experiment the gas preheat temperature was slowly increased with fixed inlet gas composition. The voltage across the catalytic filament (proportional to filament resistance, at the constant current of 1 ma) and the thermocouple voltage were simultaneously recorded. At ignition the filament temperature (and hence voltage and resistance) increases abruptly to that characteristic of the

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upper steady state. Because of the slow preheat rate and the close proximity of the gas thermocouple to the catalytic filament, the ignition temperature is taken as the gas temperature at which discontinuity of the filament resistance is observed. The gas temperature is known to ±1°C by use of a millivolt potentiometer, with 0°C reference junction, connected in parallel across the thermocouple. This procedure is then repeated for a range of C_0 values to permit use of Equation (3).

RESULTS AND DISCUSSION

Heat and Mass Transfer

Log-log plots of the heat and mass transfer functions, j_H and j_D, calculated from our own data for the C_4H_{10}-O_2 system and from the data given by Cardoso (1969) at higher flow rates, fell nicely on straight lines as a function of Reynolds number. Least squares analysis gave

$$j_H = 0.92(Re_d)^{-0.70} \tag{4}$$

$$j_D = 0.66(Re_d)^{-0.71} \tag{5}$$

The heat transfer results were in good agreement with those compiled by McAdams (1954). Although all of the data seem consistent, one caution should be kept in mind for the present application: the heat transfer coefficient is determined for relatively large ΔT values with the electrically-heated procedure described above. It may be higher than the point value appropriate to the use of Equation (3), and the calculated value of the pre-exponential Z (see below) may be correspondingly high.

Kinetic Parameter Determination

Figure 1 is a graphical presentation of the present ignition data obtained for two different catalytic wires of 0.0127-cm diam. and for a mass velocity of the butane-oxygen gas mixture of 0.1 g./cm²min.; and the ignition data reported by Cardoso (1969) for butane oxidation. Figure 1 depicts these ignition data rectified by application of Equation (3). The difference in the curves is the result of the influence of flow regime on the heat and mass transfer coefficients.

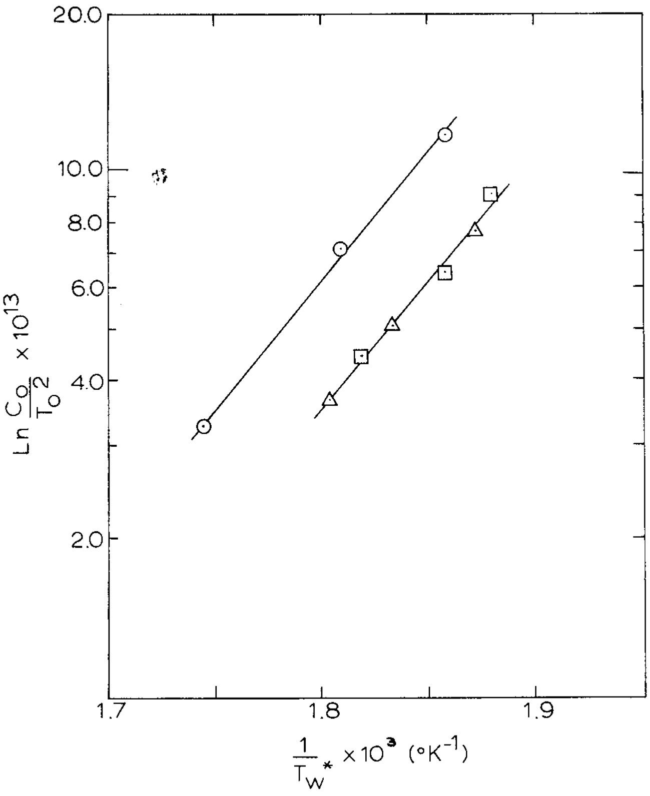

Fig. 1. Rectifying plot of $Ln(C_0/T_0^2)$ vs. $1/T_w^*$.

△ Expt. Nos. X1-X3; platinum wire #10A, 0.0127-cm diameter, 9.83-cm length, helical configuration; G = 0.1 g/cm² min.

⊡ Expt. Nos. X11-X13; platinum wire #10B, 0.0127-cm diameter, 10.21-cm length, helical configuration; G = 0.1 g/cm² min.

⊙ Data of Cardoso (1969); platinum wire, 0.0127-cm diameter, 15.6-cm length, helical configuration; G = 25.6 g/cm² min.

TABLE 1. COMPARISON OF KINETIC PARAMETERS

Method of analysis	E, kcal/g-mol	Z, cm/s	k(500), cm/s
Heated-gas; this lab	21.9 ± 1.2	3.8×10^8	0.10
Heated-gas; Cardoso (1969)	22.6 ± 1.7[a]	1.3×10^9[a]	0.18[a]
Heated-wire; this lab	20.1 ± 1.5	7.9×10^7	0.13

[a] Computed from the data of Cardoso (1969) by the present analysis.

Table 1 summarizes the kinetic parameters deduced by least squares analysis from the data plotted in Figure 1, along with the Arrhenius rate constants computed for an arbitrary temperature of 500°K. The Arrhenius parameters determined by the heated-wire technique and reported earlier by Rader and Weller (1974) are included for comparison. The uncertainty limits given for the activation energies are twice the standard deviation of the slopes of the lines in Figure 1.

The agreement in activation energies is quite reasonable for data obtained by different investigators and by two experimental techniques. The variations in pre-exponential may arise for at least two reasons: (1) there are uncertainties associated with estimating α, especially in widely different flow regimes, and the calculation of Z from the intercept of Equation (3) shows Z to be proportional to α; and (2) Z will vary with the active catalytic surface area, which may be expected to vary as the result of specific activation procedure. It is interesting that the computed first-order rate constants at an arbitrary (but plausible) temperature, 500°K, vary by less than a factor of two. This may be still another example of the compensation effect in heterogeneous catalysis (Cremer, 1955).

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