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

A new analysis is presented for the extraction of Arrhenius parameters from experimental measurements of ignition temperatures during catalytic oxidation over electrically-heated metal wires. Butane oxidation on high purity platinum wires has yielded reproducible experimental results for the reaction rate and has provided consistent estimates of the Arrhenius parameters. First-order kinetics was assumed. The present treatment contains explicit consideration of: (1) the ohmic heating term; and (2) the end conduction heat loss from the catalytic wire. The effects of wire length, diameter, and configuration are reconciled when the ignition phenomenon is referred to the center-point temperature of the wire.

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SCOPE

The existence of multiple steady states for heterogeneous chemical reaction coupled with the transport of heat and mass was analyzed by Frank-Kamenetskii (1941) for a first-order, irreversible reaction mechanism. In an extension of this early treatment, Hiam et al. (1968) made the important suggestion that the ignition phenomenon might be used to determine kinetic parameters for a first-order process. The analytical treatment was extended by Schwartz et al. (1971) to include reactions of arbitrary order.

The objective of this work was to reinvestigate the mathematical model and the experimental results for a system in which ignition occurred over an electrically-heated wire. The present method incorporates many of the practical considerations necessary for meaningful estimations of kinetic parameters for a first-order, irreversible chemical reaction catalyzed by metal wires. Specific attention is given to end conduction heat losses from the catalytic filament heated electrically, as well as to experimental determination of the effects of wire diameter, wire length, and geometric configuration of the catalytic filament on the rate of butane oxidation over high purity platinum.

This work is related to the industrial use of catalytic gauze convertors for such processes as ammonia oxidation and hydrogen cyanide production; understanding the behavior of a single catalytic wire is a first step towards design and control of the industrially important catalytic gauzes. In addition, the work holds promise for the development of a simple method to evaluate kinetic parameters quickly for a wide variety of catalytic materials and reactions.

CONCLUSIONS AND SIGNIFICANCE

Analysis and experimental measurements of the ignition phenomenon for butane oxidation on electrically-heated platinum wire have yielded Arrhenius parameters which appear to be both reproducible and independent of wire diameter, length, and configuration. A single Arrhenius plot for the first-order reaction rate constants was obtained for a series of wires of various length and diameter combinations, provided that correlation was with the computed center-point temperature of the wire rather than with the length-averaged temperature deduced from electrical measurements at the time of ignition. For the oxidation of butane on platinum wires, the activation energy was found to be 20.1 Kcal/g-mol and the pre-exponential coefficient 7.9 × 10^7 cm/s.

The internal consistency and reproducibility of the experimental results, based on the assumption of first-order kinetics, indicates that these studies can be extended in several ways: (1) the model and analysis can be extended to the treatment of *n*th order kinetics; (2) a variety of exothermic chemical reactions can be studied over a given platinum filament; and (3) a variety of catalytic surfaces can be explored, hopefully to include thin coatings of transition metal oxides on catalytically inert metal filaments.

The existence of multiple steady states for chemical reaction on a catalytic wire has been reported extensively in the literature (Liljenroth, 1918; Tammann, 1920; Davies, 1934, 1935; Buben, 1945; Hiam et al., 1968; Cardoso and Luss, 1969; Schwartz et al., 1971). The first theoretical analysis of the multiple steady state phenomenon was done by Frank-Kamenetskii (1941) for a first-order irreversible chemical reaction. This analysis was extended by Buben (1945) to include reactions of arbitrary order.

Two experimental methods have been reported in the

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literature for study of the multiple steady state phenomena associated with gaseous chemical reaction catalyzed by metal wires.

HEATED-WIRE TECHNIQUE

The heated-wire technique involves passing a reactant gas mixture at room temperature across a catalytic filament, the temperature of which is gradually increased by electrical heating. When the catalyst temperature reaches a critical value, (ignition temperature), there is a sudden transition from the lower steady state surface temperature (region of chemical reaction control) to the upper steady state (mass transfer control). Hiam et al. (1968) made the important suggestion that the kinetic parameters for first-order reactions can be deduced, using this technique, from determination of ignition temperature as a function of reactant concentration. This work was extended by Schwartz et al. (1971) to determination of the kinetic parameters for *n*th order reactions by study of ignition temperature as a function of flow rate as well as of reactant concentration. The platinum- and palladium-catalyzed oxidations of alkanes, alkenes, alcohols, and ketones were studied by this group, electrical heating of the catalytic wire being used throughout.

HEATED-GAS TECHNIQUE

The heated-gas technique involves increasing the surface temperature of the catalytic filament by flowing a preheated gas mixture across it. This method was used by Cardoso and Luss (1969) to demonstrate several pathological trends associated with multiple steady state phenomena in the oxidation of butane and carbon monoxide.

Cardoso and Luss also pointed out that the equations used by Hiam et al. (and subsequently by Schwartz et al.), in their work with the heated-wire technique, failed to include the important term for ohmic heating in the heat balance equation. Furthermore, Hiam et al. utilized a platinum wire 0.0102 cm in diameter and 2.82 cm in length, while Schwartz et al. used wires of 0.0076 cm in diameter and 5 to 8 cm in length. As Edwards, Worley, and Luss (1973) have recently shown, substantial temperature gradients can occur over the length of an electrically heated wire, and a substantial difference may exist between, say, the center-point temperature and the length-averaged temperature computed from total wire resistance.

Cardoso and Luss did not use their experimental data on butane and carbon monoxide oxidation to compute kinetic parameters. They typically operated in a turbulent flow regime, which led to the subsequent interest by Edwards et al. in the flicker phenomenon occurring during the oxidation of butane on a platinum wire. Hiam et al. and Schwartz et al. used much lower gas flow rates and were presumably operating in a laminar flow regime.

The present work constitutes a re-examination of the heated-wire technique in the study of butane oxidation over platinum. The analysis includes terms for ohmic heating and for end losses with finite wires. Experimentally, particular emphasis has been placed on the reproducibility of results and on the effects of wire length, diameter, and configuration. It appears that reproducibility can be good and that good internal consistency of rate constants, independent of wire diameter and length, can be obtained if the correlation is made with the center-point temperature of the wire at ignition rather than with the length-averaged temperature.

THEORY

The present analysis involves three assumptions:

1. The reaction is irreversible and first order with respect to hydrocarbon concentration and zero order with respect to oxygen concentration.
2. The true ignition temperature is the temperature of the center point of the electrically-heated catalytic wire.
3. The reaction involves complete combustion of butane, carbon dioxide and water being the only reaction products formed.

Assumptions 1 and 3 are based, in part, on the results reported by Moro-oka et al. (1967). They experimentally studied the oxidation of propane on supported platinum. Two significant results were reported: (1) the reaction is first order in propane concentration and independent of oxygen concentration; and (2) only carbon dioxide and water were present as reaction products. While no quantitative information has been reported on the oxidation of butane on platinum, it is not unreasonable to expect the analogous paraffins to be similar in their reaction mechanism. The value used for $(-\Delta H)$ in the subsequent treatment is that for the complete combustion of butane.

The overall steady state energy balance is

$$\begin{pmatrix}\text{Heat generated by}\\ \text{electrical energy}\end{pmatrix} + \begin{pmatrix}\text{Heat generated by}\\ \text{chemical reaction}\end{pmatrix}$$

$$= \begin{bmatrix}\text{Heat removed by con-}\\ \text{duction-convection to}\\ \text{the gas stream}\end{bmatrix} + \begin{bmatrix}\text{Heat removed by}\\ \text{axial conduction}\\ \text{in wire}\end{bmatrix}$$

Mathematically this appears

$$J[I^2R(T_w)]_R + (-\Delta H)kC = \alpha(T_w - T_0) + \frac{k_wA}{P}\left[\frac{d^2T_w}{dx^2}\right]_R \quad (1)$$

Equation (1) is subject to the following boundary conditions

$$T_w = T_0 \quad \text{at} \quad x = 0 \quad \text{and} \quad x = l_w \quad (1a)$$

In the steady state, the rate of mass transport to the surface is equal to the rate of chemical reaction; for first order kinetics,

$$kC = \beta(C_0 - C) \quad (2)$$

Elimination of C from Equations (1) and (2) leads to

$$J[I^2R(T_w)]_R + \frac{(-\Delta H)C_0}{1/k + 1/\beta} = \alpha(T_w - T_0) + \frac{k_wA}{P}\left[\frac{d^2T_w}{dx^2}\right]_R \quad (3)$$

The heat transfer coefficient α from the catalytic wire to the moving gas stream is experimentally determined by measuring the energy required to maintain the filament temperature at different values in a nonreactive atmosphere, pure oxygen.

In this case the energy balance reduces to

$$J[I^2R(T_w)]_{un} = \alpha(T_w - T_0) + \frac{k_wA}{P}\left[\frac{d^2T_w}{dx^2}\right]_{un} \quad (4)$$

Solution of Equation (4) for $\alpha(T_w - T_0)$ and combination with Equation (3) yields

$$J[I^2R(T_w)]_R + \frac{(-\Delta H)C_0}{1/k + 1/\beta} = J[I^2R(T_w)]_{un} + \frac{k_wA}{P}\left\{\left[\frac{d^2T_w}{dx^2}\right]_R - \left[\frac{d^2T_w}{dx^2}\right]_{un}\right\} \quad (5)$$

The last term in Equation (5) represents the difference in the amount of heat conducted axially through the catalytic wire in two independent experiments, each experiment being performed at the same average wire temperature: (1) through the wire exposed to a chemically reactive atmosphere (0.5 to 1.2% butane in oxygen), and (2) through the wire when it is in pure oxygen. This term is not identically zero because of some difference in the axial temperature distribution with and without chemical reaction. However, the term should be small, particularly at the ignition point (with which this paper is concerned), and it will be neglected in the subsequent development. With this assumption, Equation (5) may be rewritten

$$\frac{(-\Delta H)C_0}{1/k + 1/\beta} = J\{[I^2R(T_w)]_{un} - [I^2R(T_w)]_R\} \quad (6)$$

If the mass transfer coefficient β is independently determined, Equation (6) permits calculation of the first-order rate constant k from experimentally measured quantities.

Equation (6) is characterized by two stable regions in temperature. The lower regime is that where chemical reaction limits the rate, and $k < \beta$. The upper regime is that of mass transfer control, $k > \beta$. For conditions of mass transfer control, Equation (6) can be approximated

$$\beta(-\Delta H)C_0 = J\{[I^2R(T_w)]_{un} - [I^2R(T_w)]_R\} \quad (7)$$

Thus the upper thermal regime provides a physical situation whereby the mass transfer coefficient β can be determined from experimentally measured variables. The simplified form of the overall energy balance represented by Equation (7), which is dependent on the assumption that $k >> \beta$ in the upper steady state, will be further justified below.

EXPERIMENT

Apparatus

The experimental apparatus used in this work consists of a catalytic filament connected in series with a high precision (1%) electrical resistor (0.1 ohm) and a Hewlett-Packard model 6443B d.c. power supply. The filament, arranged in one of several geometric configurations, is positioned horizontally inside a 4.13-cm diameter stainless steel reactor and supported by two 0.125-cm diameter stainless steel rods. The reactant gas mixture is prepared by metering oxygen and butane separately through calibrated rotameters to a mixing chamber of stainless steel baskets and is then passed axially through the reactor and normal to the catalytic wire. Platinum wires of 99.99+ % purity, purchased from United Mineral and Chemical Corporation, were used as catalyst.

A Hewlett-Packard model 7100B dual channel strip chart recorder was used to simultaneously record the voltage across the catalytic filament and the voltage across the high precision resistor.

Procedure

The initial and least understood aspect of the experimental procedure involves activation of a fresh catalytic wire. Cortez (1968) has qualitatively described the catalytic activity of platinum oxidation catalysts as a complicated function of their physical, mechanical, chemical, and thermal history. Satterfield and Cortez (1970) have reported prolonged pickling in concentrated HCl to be the best method for activation of platinum screens for the oxidation of hexene or toluene in excess air. Edwards et al. (1973) effected activation by electrically heating platinum wires to 600° to 800°C in air. We have activated new wires, apparently reproducibly (see Figure 3 below), by heating them electrically to approximately 800°C in a 1% butane-99% oxygen gas mixture for about 25 min. Scanning electron micrographs show that this treatment markedly increases the surface roughness of the wire.

After activation, the heat transfer characteristics are determined by passing pure oxygen, at known linear velocity, normal to the wire. The energy required to maintain the platinum filament at various temperatures provides a measure of the heat transferred to the flowing gas stream.

The mass transfer characteristics are determined by observing the difference in the energy required to maintain the catalytic filament at various temperatures for a wire upon which chemical reaction is taking place and for the same wire in pure oxygen. Data for mass transfer are taken only in the upper temperature regime, where mass transfer is rate-limiting.

The transition from the region of chemical reaction control to the region of mass transfer control is signaled by an abrupt change in the temperature (and resistance) of the catalytic wire. To determine the nominal ignition temperature $\overline{T}_w^*$ corresponding to a given butane concentration, the electrical energy supplied to the wire is gradually increased until this abrupt change is observed. At constant linear gas velocity, this procedure is repeated with different butane concentrations so that the ignition temperatures are determined for a range of reactant concentrations. A value of the mass transfer coefficient, determined at higher temperatures and extrapolated to each desired ignition temperature, then provides a means for determination of the first-order reaction rate constants for a range of butane concentrations and ignition temperatures. Knowledge of k as a function of temperature permits determination of the Arrhenius parameters.

In these experimental measurements, the resistance of the catalytic filament is calculated by simultaneously measuring the voltage across the filament and the current through it. The nominal (or average) temperature of the wire ($\overline{T}_w$) is then determined from the resistance-temperature characteristics of platinum according to the following relation:

$$R(\overline{T}_w)/R_0 = 1.0 + 3.981 \times 10^{-3}\overline{T}_w - 5.849 \times 10^{-7}\overline{T}_w^2 \quad (8)$$

The wire filament thus serves the three purposes of catalyst, indicator of ignition, and temperature transducer.

Developing further the work of Hinze (1959), Edwards et al. (1973) have shown that the temperature distribution along a wire heated electrically is given by

$$\frac{T_w - T_0}{\overline{T}_w - T_0} = \frac{1.0 - \cosh(\lambda s)/\cosh\lambda}{1.0 - \tanh\lambda/\lambda} \quad (9)$$

where

$$s = 2(x - x_c)/l_w \quad (9a)$$

$$\lambda = \frac{l_w\{MI^2R_0\gamma[R(T_0) - \eta R(\overline{T}_w)]\}^{1/2}}{d_w\{l_w k_w \pi[R(\overline{T}_w) - R(T_0)]\}^{1/2}} \quad (9b)$$

and the fractional end conduction loss is defined:

$$\eta = \frac{\pi k_w d_w^2 \lambda \tanh\lambda(\overline{T}_w - T_0)}{MI^2R(\overline{T}_w)l_w(1.0 - \tanh\lambda/\lambda)} \quad (9c)$$

Equation (9) has been derived for the following boundary conditions:

$$T_w = T_0 \quad \text{at} \quad x = 0 \quad \text{and} \quad x = l_w \quad (10)$$

The values of λ and η can be determined by iterative solution of Equations (9b) and (9c). Edwards et al. further show the average and center temperature of the wire to be related:

$$\frac{T_{cp} - T_0}{\overline{T}_w - T_0} = \frac{\lambda\cosh\lambda - \lambda}{\lambda\cosh\lambda - \sinh\lambda} \quad (11)$$

Edwards et al. have measured several axial temperature profiles by micro-optical pyrometry and report excellent agreement between the experimental results and the theoretical predictions from Equation (9).

EXPERIMENTAL RESULTS

Heat and Mass Transfer

Figure 1 represents a typical heat transfer curve for a 0.0127-cm diam., helically-coiled platinum wire. Temperatures for this figure are calculated by Equation (8), while the power input $[I^2R(\overline{T}_w)]$ is measured directly. Figure 2 depicts the corresponding mass transfer coefficient calculated according to Equation (7) as a function of nominal wire temperature for the same system.

Reproducibility of Results

Figure 3 presents results of four separate groups of experiments in the form of nominal ignition temperature as a function of bulk phase composition for (1) the same wire on the same day, that is, consecutive experimental runs, (2) the same wire on subsequent days, and (3) two separate wires of similar length taken from the same spool of platinum wire.

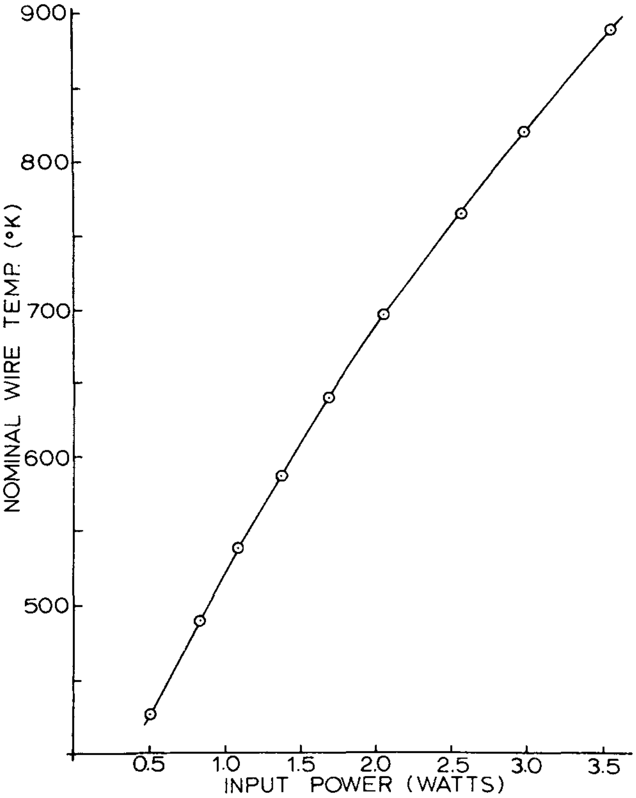

Fig. 1. Nominal wire temperature vs. power input. Platinum wire #4A, 0.0127-cm diam., 10.97-cm length, helical configuration; $\overline{v}$ (pure oxygen) = 1.34 cm/s.

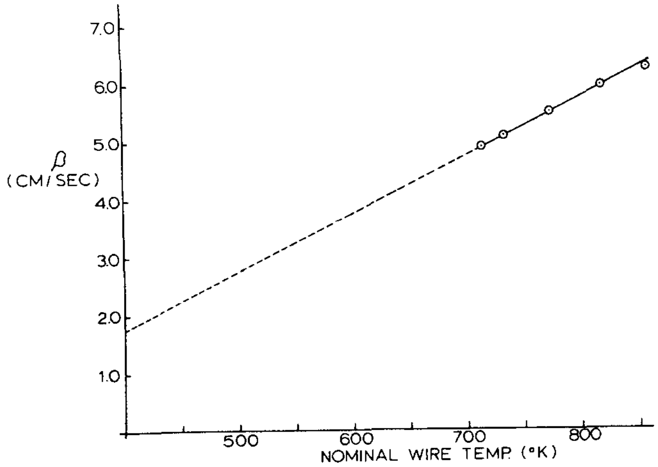

Fig. 2. Mass transfer coefficient vs. nominal wire temperature. Platinum wire #4A, 0.0127-cm diameter, 10.97-cm length, helical configuration; $\overline{v}$ (0.69% butane-99.31% oxygen) = 1.34 cm/s.

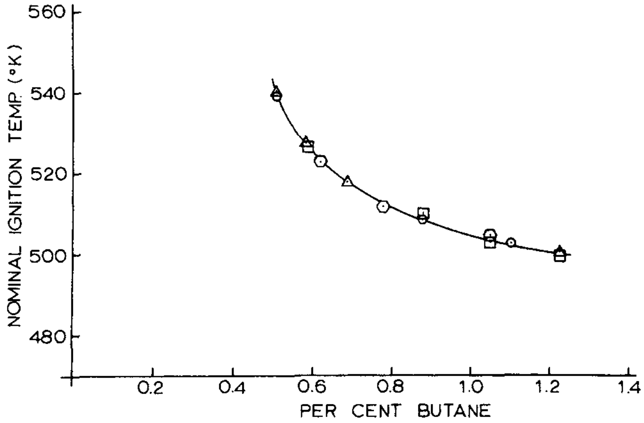

Fig. 3. Reproducibility: Nominal ignition temperature vs. bulk phase composition. △—Expt. Nos. I11-I14; Platinum wire #7B, 0.00762-cm diam., 9.61-cm length, helical configuration; $\overline{v}$ = 1.34 cm/s.; ⬡—Expt. Nos. I15-I17; Platinum wire #7C, 0.00762-cm diam., 9.82-cm length, helical configuration; $\overline{v}$ = 1.34 cm/s.; ⊙—Expt. Nos. I18-I110; Platinum wire #7C, 0.00762-cm diam., 9.82-cm length, helical configuration; $\overline{v}$ = 1.34 cm/s.; and ⊡—Expt. Nos. I111-I114; Platinum wire #7C, 0.00762-cm diam., 9.82-cm length, helical configuration; $\overline{v}$ = 1.34 cm/s.

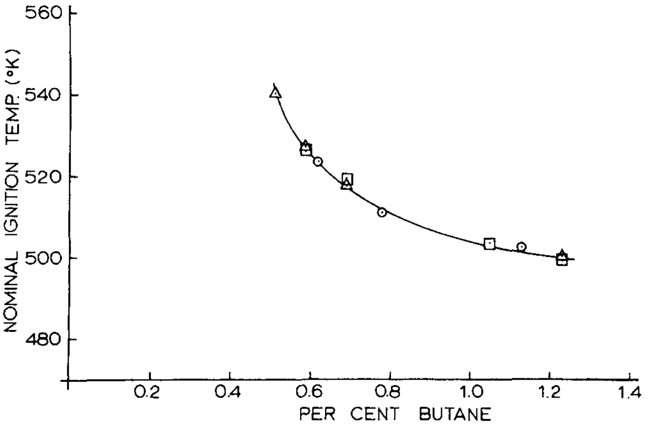

Fig. 4. Configuration effect: Nominal ignition temperature vs. bulk phase composition. △—Expt. Nos. II11-II14; Platinum wire #7B, 0.00762-cm diam., 9.61-cm length, helical configuration; $\overline{v}$ = 1.34 cm/s.; ⊙—Expt. Nos. II15-II17; Platinum wire #7D, 0.00762-cm diam., 10.04-cm length, straight configuration; $\overline{v}$ = 1.34 cm/s.; and ⊡—Expt. Nos. II18-II111; Platinum wire #7D, 0.00762-cm diam, 10.04-cm length, hairpin back-and-forth configuration; $\overline{v}$ = 1.34 cm/s.

Effect of Wire Configuration

Figure 4 illustrates the results obtained for two different wires of similar length and equal diameter but arranged in three different geometric configurations. One wire was coiled into a helix of 0.159-cm diam., the second wire was positioned as a single loop between the support rods; this same wire was also arranged in a flat, hairpin back-and-forth design. The nominal ignition temperatures vs. gas phase concentrations are shown in Figure 4.

Length and Diameter Effects

Table 1 lists experimental data for the nominal ignition temperatures as a function of butane concentration at constant linear gas velocity for various wires. Also in-

TABLE 1. IGNITION DATA AND KINETIC RATE CONSTANTS

Expt. no.	Wire Description	Butane conc., % C_4H_{10}	Nominal ignition temp., °K	Wire center temp., °K	k, cm/s
IV1	d_w = 0.00762 cm	0.585	528	545	0.71
IV2	l_w = 9.61 cm	0.690	518	535	0.47
IV3		1.230	501	516	0.23
V1		0.585	536	549	0.78
V2	d_w = 0.00762 cm	0.780	518	529	0.38
V3	l_w = 17.15 cm	1.050	510	521	0.30
V4		1.230	506	517	0.25
VI1	d_w = 0.0127 cm	0.460	496	516	0.22
VI2	l_w = 10.97 cm	0.710	470	487	0.09
VI3		1.130	463	479	0.05
VII1		0.585	489	504	0.14
VII2	d_w = 0.0127 cm	0.660	482	496	0.10
VII3	l_w = 17.77 cm	0.780	478	492	0.08
VII4		1.230	470	481	0.06

cluded in Table 1 are the corresponding center temperatures of each wire calculated from Equation (11) and the Arrhenius rate constants k calculated from Equation (6).

In these experiments, the difference between T_{cp}^* and $\overline{T}_w^*$ fell in the range 11° to 20°C; as would be expected, $(T_{cp}^* - \overline{T}_w^*)$ decreased with increasing wire length and decreasing wire diameter.

Figure 5 graphically represents the nominal ignition temperatures vs. bulk gas phase composition for the data of Table 1.

Axial Temperature Distribution

Figure 6 depicts a typical axial temperature distribution, calculated from Equation 9, in this case for the ignition condition in Experiment No. VI3, Table 1. Also indicated in this figure is the experimentally-determined nominal or average temperature of this same wire deduced from its measured resistance.

Arrhenius Rate Constant Data

Figure 7 represents the Arrhenius rate constants determined from Equation (6) for the ignition data of Table 1. In this figure the values of ln k are plotted against $1/\overline{T}_w^*$.

Figure 8 represents the same Arrhenius rate constants, but plotted as ln k against $1/T_{cp}^*$. All points except that for Experiment No. VI2 fall reasonably well on a single line. Least squares analysis of the data in Figure 8 yields an activation energy, E = 20.1 kcal/g-mol, and a preexponential coefficient, $z = 7.9 \times 10^7$ cm/s.

Discussion

The heated-wire technique for studying ignition at a catalytic surface is an experimentally attractive approach for the determination of kinetic parameters. Even with the restriction to first-order kinetics, however, two conditions must be satisfied in order to obtain meaningful results: (1) the term for ohmic heating of the catalytic filament must be explicitly included in the heat balance equation; and (2) the wire center-point temperature, rather than the nominal temperature deduced from mea-

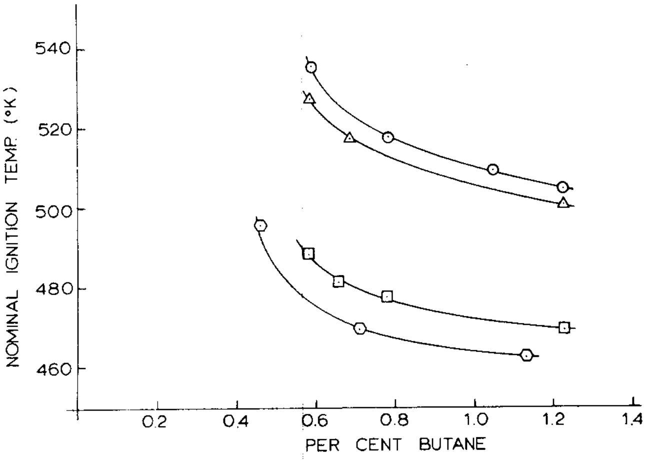

Fig. 5. Length and diameter effects: Nominal ignition temperature vs. bulk phase composition. △—Expt. Nos. IV1-IV3; Platinum wire #7E, 0.00762-cm diam., 9.61-cm length, helical configuration; $\bar{v}$ = 1.34 cm/s.; ⊙—Expt. Nos. V1-V4; Platinum wire #7F, 0.00762-cm diam., 17.15-cm length, helical configuration; $\bar{v}$ = 1.34 cm/s.; ⊖—Expt. Nos. VI1-VI3; Platinum wire #7G, 0.0127-cm diam, 10.97-cm length, helical configuration; $\bar{v}$ = 1.34 cm/s.; and ⊡—Expt. Nos. VII1-VII4; Platinum wire #7H, 0.0127-cm diam., 17.77-cm length, helical configuration; $\bar{v}$ = 1.34 cm/s.

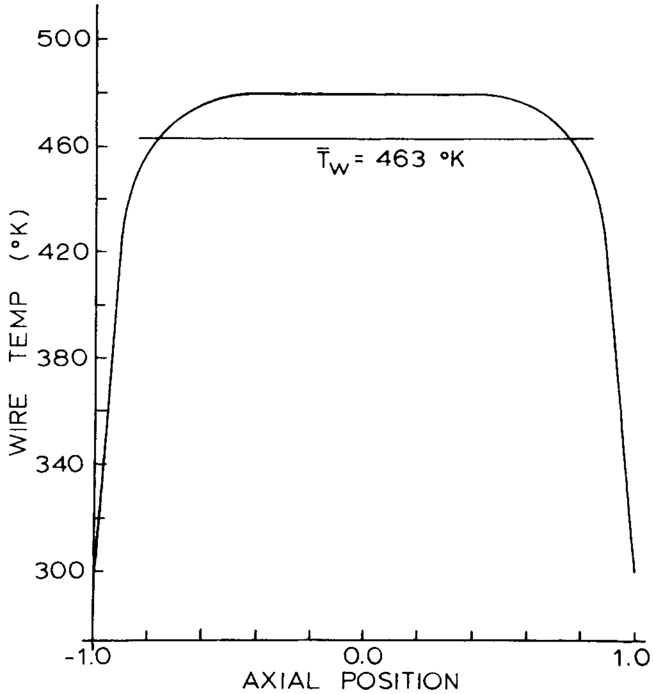

Fig. 6. Axial temperature distribution: Wire temperature vs. dimensionless axial position.

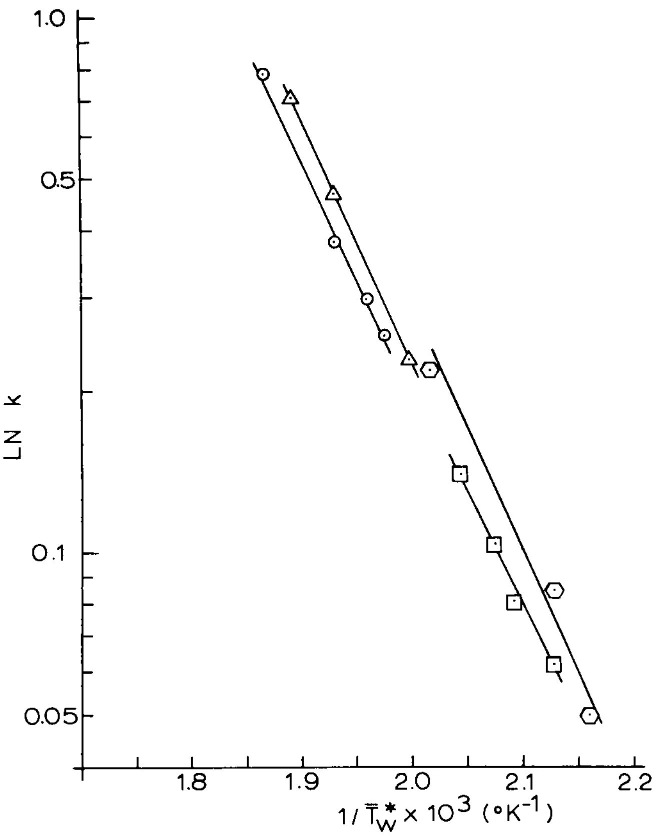

Fig. 7. Arrhenius rate data: Ln *k* vs. reciprocal ignition temperature (nominal).

sured resistance, should be employed in the Frank-Kamenetskii equations. The first condition is obvious. The importance of the second depends on the magnitude of the heat end loss, which in turn depends on the wire diameter and length; the validity of this condition is further discussed below.

Figure 5 illustrates the effects of diameter and length on the nominal ignition temperature as a function of bulk phase composition. Qualitatively the effect of using a catalytic wire of the same diameter but greater length should be to decrease the influence of end conduction heat loss. A wire of infinite length will have a truly uniform axial temperature; therefore, increasing wire length will tend to flatten the temperature profile of the central portion of the catalyst. This has been elegantly demonstrated by Edwards et al. (1973). Figure 5 is consistent with this fact. The curves for the longer wires indicate that a higher nominal ignition temperature $\overline{T}_w^*$ is required for the same bulk phase concentration and linear velocity. This occurs because the longer wires have more uniform temperature profiles over the center portion of the wire than the shorter wires, and the computed values of $\overline{T}_w^*$ for the longer wires more closely approach the true ignition temperatures.

The effect of wire diameter on the nominal ignition temperature is also shown in Figure 5. The amount of heat per unit area transferred by conduction-convection to the flowing gas stream is greater for a smaller diameter wire under the same conditions of flow. The data in Figure 5 are consistent with this fact; the nominal temperatures of ignition for the 0.00762-cm diam. wires are higher than those for the 0.0127-cm diam. filaments because of the higher heat transfer coefficient associated with the smaller diameter wires.

Figure 4 illustrates the effect of wire configuration on nominal ignition temperature. The use of a helical configuration is typically preferred for the reasons that a longer wire can be used for a given distance between support rods, and the effect of mechanical vibration of the wire is minimized. Vibration proved not to be an important consideration for the low flow rates used in the present study. It was anticipated that a helical configuration might be a complicating factor in the fluid dynamics of a catalytic wire system. However, Figure 4 indicates that the wire configuration is not important in the flow regime studied.

Our own results have proved unexpectedly reproducible since scanning electron microscopy showed marked surface roughening and development of surface striations to occur on activation. The reproducibility is illustrated by the four groups of experiments shown in Figure 3, in which the nominal ignition temperature is plotted against butane concentration. Two of these experimental groups were performed with the same wire and on the same day; another set of data is for this same wire on the subsequent day; the fourth set of data was obtained from a different piece of wire. All experiments were preceded by the identical activation procedure.

As previously mentioned, the method for determining the mass transfer coefficient β relies on the supposition that in the upper steady state $k >> \beta$. The adequacy of this assumption can be illustrated by noting in Figure 2 that β at 715°K (for example) is 4.9 cm/s. From the kinetic parameters determined by the present analysis, $k_{715^\circ K}$ is computed to be 56.7 cm/s. Thus the error introduced by the simplification of Equation (6) into the form of Equation (7) for the upper steady state is small. Furthermore, calculation of the rate constant k is quite insensitive to the value of the mass transfer coefficient. For example: Experiment No. VII, Table 1, shows $k = 0.22$ cm/s, computed from the value of $\beta = 2.8$ cm/s, obtained

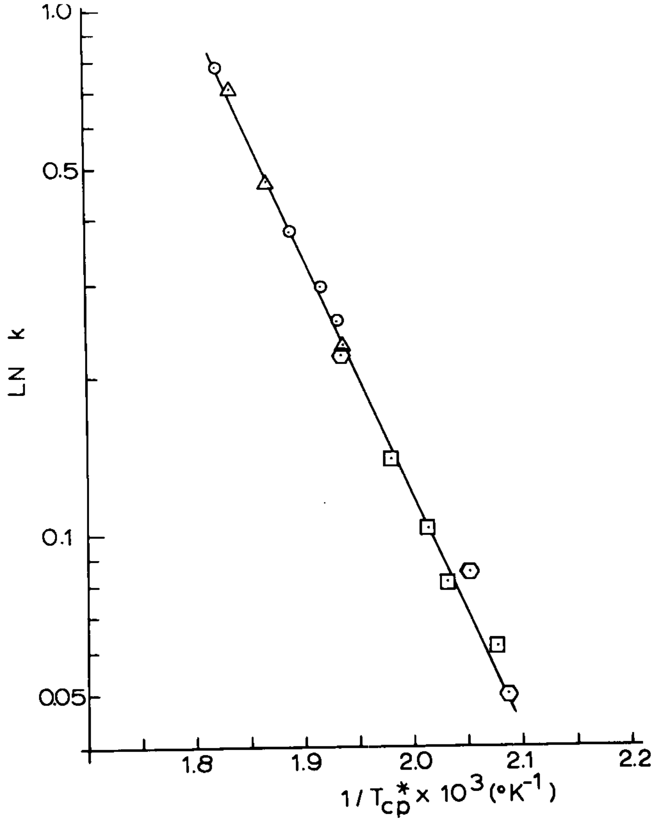

Fig. 8. Arrhenius rate data: Ln *k* vs. reciprocal ignition center-point temperature.

by extrapolation of the data in Figure 2 to the nominal ignition temperature of 496°K. However, even for $\beta = 1.8$ cm/s (extrapolation to 400°K in Figure 2), k is found to be 0.23 cm/s; and for $\beta = \infty$ (no mass transfer resistance), $k = 0.20$ cm/s.

Figure 6 illustrates the calculated temperature profile based on Equation (9) for the condition of ignition in Experiment No. VI3, Table 1. This figure graphically illustrates the impropriety in assuming that the temperature of ignition is the nominal or average temperature deduced from the average resistance of any particular wire. This conclusion is further substantiated in Figure 7, in which four separate Arrhenius plots result from the use of four different wires of various diameter and length combinations when the correlation is with nominal ignition temperature.

It is perhaps axiomatic to state that the true temperature of ignition should be that of the center point, the hottest point with a finite wire, when ignition first occurs. It was not feasible in the present work to measure the center-point temperature directly. On the basis of the work of Edwards et al., however, calculation of the temperature profile and center-point temperature, with the use of Equations (9) and (11) and the experimental measurements at the ignition point, seems reliable. In any event, when ignition occurs it is much more plausible to postulate that the true ignition temperature is that at the center point than to use the nominal or average temperature. The fact that a single Arrhenius plot, for two wire diameters and two lengths, was obtained in Figure 8 with the use of the center-point temperature gives credence to this assumption. A caveat should be added; although this postulate is physically plausible and leads to internally consistent results for the wires studied, the results reported do not guarantee that extrapolation, say, to extremely short wires will necessarily prove valid.

The use of the calculated wire center-point temperature as the true temperature of ignition requires some further discussion. The basic equations for the wire temperature distribution are derived for conditions of no surface chemical reaction. Justification for the use of Equation (9) to compute the true ignition temperature in a reactive gas comes from the fact that the ohmic heating term is the dominant term in the total energy balance. Up to and including the point of ignition, the rate is limited by chemical reaction control. This implies small conversion of reactant species, $C \simeq C_0$, and small heat generation by the exothermic surface reaction. The contribution by chemical reaction to the rise in temperature of the catalytic wire is therefore insignificant in comparison to ohmic heating.

In addition, the temperature distribution derived from Equation (9) is dependent on experimentally determined parameters I and $R(\overline{T}_w)$ which are measured for conditions of ignition. This fact provides incremental compensation for the influence of surface chemical reaction in the computation of the temperature distribution.

CONCLUSIONS AND REMARKS

The work here presented was intended to develop a sound method for determining kinetic parameters by the heated-wire technique. The internal consistency of the results obtained to date indicates that the method is a straightforward tool for this purpose.

The present method of analyzing ignition data obtained with the heated-wire technique has the following characteristics: (1) The general energy balance equation includes terms for the ohmic generation of heat within the catalytic wire and for conduction end losses; (2) The resistance due to mass transfer is included in the phenomenological representation; (3) An internal means is provided for diminishing the error associated with axial heat conduction within the wire; and (4) The true ignition temperature is taken to be the center-point temperature of the catalytic wire.

Work is currently underway to develop a method for determining kinetic parameters for systems of arbitrary reaction order.

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NOTATION

A = cross section of wire, cm^2
C = concentration of reactant species at catalyst surface, g-mol/cm^3
C_0 = concentration of reactant species in bulk stream, g-mol/cm^3
d_w = wire diameter, cm
E = activation energy, cal/g-mol
$(-\Delta H)$ = heat of reaction, cal/g-mol
I = current through catalytic wire, amps
J = conversion factor, cal/cm^2 s watt
k = first-order reaction rate constant, cm/s
k_w = thermal conductivity of catalytic wire, cal/cm s °K
l_w = length of wire, cm
M = conversion factor, cal/s watt
P = perimeter of wire, cm
R = gas constant, cal/g-mol °K
R_0 = resistance of catalytic wire at 0°C, ohm
$R(T_0)$ = resistance of catalytic wire at bulk gas temperature, ohm
$R(\overline{T}_w)$ = resistance of catalytic wire at average wire temperature, ohm
s = dimensionless axial position defined by Equation (9a)
T_0 = bulk gas temperature, °K
T_{cp} = center point temperature of catalytic wire, °K
T_{cp}^* = center point temperature of catalytic wire at ignition, °K
T_w = temperature of catalytic wire, °K
$\overline{T}_w$ = average or nominal temperature of catalytic wire, °K
$\overline{T}_w^*$ = average or nominal ignition temperature of catalytic wire, °K
x = axial distance along wire, cm
x_c = position of wire center point, cm
z = pre-exponential coefficient, cm/s

Greek Letters

α = heat transfer coefficient, cal/cm^2 s °K
β = mass transfer coefficient, cm/s
γ = temperature coefficient of resistance, 1/°K
η = fractional end conduction heat loss, defined by Equation (9c)
λ = quantity defined by Equation (9b)

Subscripts

R = quantities measured in reactive gas mixture
un = quantities measured in non-reactive atmosphere

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Sorption and Diffusivity Characteristics of Acid-Leached Mordenites

The apparent diffusivity for the binary liquid systems benzene-cumene and cyclohexane-cumene in H-mordenite crystals at 25°C to 44°C was increased by an order of magnitude or more after the zeolite was acid-leached to increase the silica-alumina mole ratio from the range of 14 to 18 to the range of 70 to 89. The calculated diffusivities, which range from 10^{-12} to 10^{-16} cm^2/s, decrease with approach to sorption equilibrium and may be markedly reduced under some circumstances by adsorption of molecules from the bulk liquid, causing blockage of pores.

Comparison of sorption capacities as a function of silica-alumina ratio as reported by various investigators indicates that considerable differences exist in the properties of acid-leached mordenites of the same silica-alumina ratio but of different origins.

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SCOPE

H-mordenite and acid-leached mordenites have remarkable catalytic activities for acid-catalyzed reactions, but the rate and selectivity of these reactions can be profoundly affected by the rate of counterdiffusion of product and reactant molecules inside the fine pore structure of these zeolites. Acid leaching removes alumina from the silica-alumina matrix and opens up the pores of mordenites, thereby increasing the rate of diffusion. However, leaching also reduces the concentration of acid sites, thereby presumably decreasing the intrinsic reactivity of the catalyst. The two effects act in opposite directions on the apparent reactivity of the mordenite under diffusion-limiting conditions.

A principle objective of this work was to determine quantitatively the effect of acid leaching on diffusivity in mordenites. Diffusion measurements were made by observing the rate of disappearance of a hydrocarbon species A by adsorption from a dilute solution of A in B into mordenite crystals previously saturated with B—termed here *adsorption measurements*; or by observing the rate of appearance of B from saturated mordenite into bulk liquid consisting initially of pure A—termed here *desorption measurements*.

Sorption capacities for benzene or cumene vapors were also determined as a function of silica-alumina ratio and compared to previous reports on sorption of these and other hydrocarbons. Sorption capacities are of interest in themselves in connection with adsorption processes, and they also provide some insight into the nature of the fine pore structure.

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