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Catalytic Oxidation of Hydrocarbons on Platinum*

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The catalytic oxidation of several hydrocarbons on a platinum filament has been examined. From a study of the conditions required for heterogeneous thermal ignition, the rates of oxidation of several paraffins were determined. The influence of chemical structure of the hydrocarbon molecule on the catalytic process is discussed.

INTRODUCTION

The catalytic oxidation of hydrocarbons on metal surfaces is of considerable importance to the chemical industry. Yet relatively little published information is available on the relationship between hydrocarbon structure and the kinetics and mechanism of the heterogeneous reactions. A review by Dixon and Longfield (*1*) discussed catalytic studies carried out on metallic oxides and metals covered with stable oxide layers. The work by Kemball and co-workers (*2, 3*) concerned the oxidation of ethylene and substituted olefins on evaporated films of palladium and platinum and a comparison of these rate data with those observed for rhodium, gold, and tungsten films. The results indicated that the predominant reaction at temperatures less than 140°C is complete oxidation to carbon dioxide and water. Some oxidation studies of methane at catalyst temperatures in excess of 1000°C have been carried out by Prettre and co-workers (*4*).

The objective of our work is to compare the catalytic oxidation of a homologous series of hydrocarbons on platinum. The results of these measurements are described in this report. Subsequent studies will be concerned with similar investigations on different metal surfaces.

The experimental approach is based on the principle of "thermal ignition" by exothermic heterogeneous reaction as developed by Frank-Kamenetskii (*5*). The principle of this technique has been applied to the study of the catalytic oxidation of hydrogen and ammonia (*6*).

THEORETICAL ANALYSIS

The analysis that follows is essentially that developed in ref. (*5*). In the mathematical theory of heterogeneous ignition, the steady state mass flux of reactant to a catalytic surface (*7*) is given by

$$\varphi = \frac{n}{(1/k) + (1/\beta)} \tag{1}$$

for a surface reaction of first order in hydrocarbon concentration and zero order in oxygen concentration, as appears to apply to catalytic hydrocarbon oxidation under the experimental conditions chosen (*2*), i.e., in a large excess of O_2. In Eq. (1), k is the catalytic rate constant, n the bulk concentration of reactant, and β is a diffusivity term defined by $\beta \equiv Nu(D/d)$, where Nu is a Nusselt number, D is a diffusion coefficient, and d is a characteristic linear dimension of the system.

The net flux of heat generation on the filament due to exothermic heterogenous reaction is

$$\dot{q}_1 = \varphi Q = \frac{Qn}{(1/k) + (1/\beta)} \tag{2}$$

where Q is the enthalpy of the reaction.

For conductive heat loss to the surrounding gas, the heat flux from the filament is

$$\dot{q}_2 = \alpha(T - T_0) \tag{3}$$

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where α is the heat transfer coefficient, and $T - T_0$, the temperature difference between the filament and incoming gas. When $\dot{q}_1 = \dot{q}_2$, a stationary state in temperature is reached, and at this point

$$\frac{Qn}{(1/k) + (1/\beta)} = \alpha(T - T_0) \qquad (4)$$

For the condition $E/RT \gg 1$ and $(T - T_0) < T_0$, the Arrhenius rate constant $k = Z \exp(-E/RT)$ can be approximated (5) by $k \cong [Z \exp(-E/RT_0)] \{\exp[E(T - T_0)/RT_0^2]\}$. On introduction of this relationship into Eq. (4) and rearrangement, one obtains

$$\frac{Qn}{\alpha} \frac{EZ}{RT_0^2} \exp\left(-\frac{E}{RT_0}\right) = \frac{E(T - T_0)}{RT_0^2} \times \left\{\frac{Z}{\beta} \exp\left(-\frac{E}{RT_0}\right) + \exp -\left[\frac{E(T - T_0)}{RT_0^2}\right]\right\} \qquad (5)$$

This function of T has two stable stationary states. Of special interest is the point of transition from the kinetically controlled regime [$\beta > k$, cf. Eq. (1)] to the diffusion-controlled regime [$\beta < k$, cf. Eq. (1)], since it represents the unstable stationary state related to ignition.

The critical condition for ignition, designated by an asterisk, may be found by differentiating the right side of Eq. (5) and setting the result equal to zero. Thus one finds

$$\left(\frac{E\alpha}{QZRT_0^2}\right) \left[\frac{(T^* - T_0)^2}{n}\right] = \exp\left(\frac{-E}{RT^*}\right) \qquad (6)$$

or,

$$\left(\frac{E}{RT^*}\right) = \ln \left[\frac{n}{(T^* - T_0)^2}\right] + \ln \left(\frac{QZRT_0^2}{E\alpha}\right) \qquad (7)$$

It is apparent from Eq. (7) that by means of graphical analysis the activation energy for the first order catalytic process may be evaluated. Thus, a plot $\ln[n/(T^* - T_0)^2]$ versus $1/T^*$ should lead to a straight line of slope E/R. Furthermore, measurement of the heat transfer coefficient allows quantitative analysis of the pre-exponential coefficient in the Arrhenius equation if the heat of combustion is known.

Experimental Details

The experimental apparatus used in this work consists of a Wheatstone bridge composed of two metal filaments, one located in the gas sample stream and the other a reference filament located in hydrocarbon-free O_2. The remainder of the bridge is composed of two fixed resistors and a zero-adjust potentiometer. A regulated variable voltage power supply provides direct current for exciting the bridge and heating the platinum filaments. An x–y recorder displays the bridge output signal on the y axis and the current through the filaments, which is related to their temperature, on the x axis.

The samples are prepared by metering hydrocarbon and O_2 through calibrated rotameters to a Raschig-ring-packed mixing chamber and then to the detector through flow-adjusting needle valves.

The parameter measured is the ignition temperature as a function of reactant concentration for various hydrocarbon–O_2 mixtures. The procedure employed is to meter the gas sample at a constant flow rate of 30 cc/min over the platinum filament and gradually to increase the filament temperatures by joule heating until exothermic reaction is initiated. This event is signaled by an abrupt change in the bridge output voltage. The temperature of the active filament at the point of ignition is related to the filament current at ignition through a calibration technique that entails measuring the filament resistance as a function of filament current and utilization of the known temperature-resistance function of the metal. The filament thus serves the threefold purpose of catalyst, indicator of ignition, and temperature transducer. The catalyst filaments (manufactured by Johnson-Williams Company, Mountain View, California) were made of platinum (0.004 inch in diameter, 1.11 inch in length, coiled into a helix of 0.018 inch diameter; purity 99.99%). Detailed analysis of the data indicated that up to the ignition point the heat release, due to chemical reaction, is small relative to the joule heating for the gas mixtures employed in our measurements. As can be seen from the data presented in Table 1 the gas mix-

TABLE 1
CONCENTRATION DEPENDENCE OF CATALYTIC IGNITION TEMPERATURES

Hydrocarbon concentration (mole fraction × 10^3)		Ignition temperature (°K)
Butane	4.2	500°
	7.4	473°
	12.0	463°
	18.7	453°
Propane	5.2	558°
	10.3	523°
	16.8	505°
	23.1	493°

tures contained large amounts of oxygen, well in excess of the stoichiometric requirements.

The ignition temperature as a function of hydrocarbon concentration was evaluated for four separate systems. Detailed data for propane and butane are given in Table 1. In accordance with Eq. (7), the results of these measurements are analyzed graphically in Fig. 1. From the slope of these lines the activation energy for the catalytic oxidation process was computed. In addition by means of Eq. (6) the pre-exponential factors were calculated (Table 2).

DISCUSSION

The procedure described here allows rapid determination of the rates of catalytic oxidation and a convenient method for comparison of the reactivity of different hydrocarbons. For the series of paraffins studied the catalytic oxidation rate over platinum has been computed at 500°K (Table 3). The rate constants exhibit a marked increase in going from C_2H_6 to C_4H_{10}. Also the role of a side chain in oxidation rate is apparent from a comparison of butane with isobutane. In the case of propane the activation energy derived from our measurements is similar to that obtained by Morooka and co-workers on a supported platinum catalyst (*8*). Also, the orders of the reaction with respect to propane and oxygen are in agreement with the kinetic parameters reported by these authors.

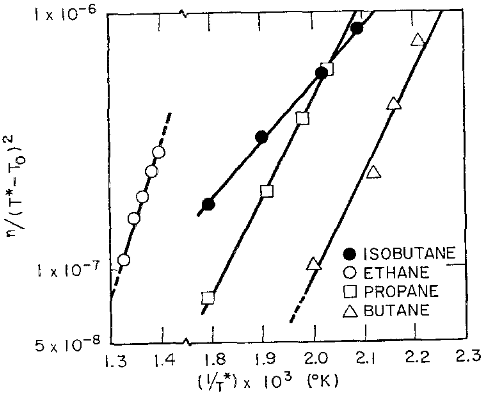

FIG. 1. Variation in catalytic ignition temperature with gas composition.

TABLE 2
KINETIC DATA FOR HYDROCARBON OXIDATION CATALYZED BY PLATINUM

Hydrocarbon	Pre-exponential term (cm sec^{-1})	Activation energy (kcal $mole^{-1}$)
C_2H_6	2.8×10^{10}	27.3
C_3H_8	1.1×10^9	17.0
C_4H_{10}	3.3×10^9	17.0
iso-C_4H_{10}	4.6×10^5	10.2

In recent publications the strength of the metal–oxygen bond has been considered as a governing factor in hydrocarbon oxidation. A variety of correlations have been presented in which catalytic oxidation activity was related to the ease of rupture of the oxygen–catalyst bond (*8–10*). From our experimental results it is apparent that the nature of the hydrocarbon molecule must also be taken into consideration. The degree of coverage of the catalyst surface with oxygen is expected to be incomplete (*10, 11*). One may speculate on the possibility of

TABLE 3
REACTION RATE CONSTANT FOR CATALYTIC OXIDATION AT 500°K

Hydrocarbon	Rate constant (cm sec^{-1})	Relative rate	
		Heterogeneous	Homogeneous[a]
C_2H_6	4.7×10^{-2}	1	1
C_3H_8	46	9.8×10^2	1×10^2
C_4H_{10}	140	3.0×10^3	5×10^2
iso-C_4H_{10}	17	3.6×10^2	—

[a] Reference (*14*).

alkane chemisorption on that portion of the surface which is oxygen-free, followed by reaction with a mobile layer of chemisorbed oxygen. On the basis of our experiments it would be difficult to distinguish between such a mechanism and one in which alkane adsorption takes place on top of a chemisorbed oxygen layer. In the latter case changes in hydrocarbon structure as well as in type of metal catalyst would be expected to have a minor effect on catalytic reactivity. On the other hand, dissociative chemisorption of the different paraffin molecules on the bare portion of the platinum surface should lead to marked variations in the bonding energies of the adsorbate to the metal atom of the lattice (*12*). Although the process of dissociative adsorption leads to the formation of strongly bonded species, the presence of co-adsorbed oxygen results in their rapid oxidation. Such a mechanism is in line with our studies on oxidative dehydrogenation (*13*), in which it was noted that an oxygen-poor surface can be readily poisoned by the hydrocarbon residue resulting from hydrogen abstraction by the transition metal. The differences in activation energy undoubtedly reflect the differences in the dissociation energy of the C—H bond broken during the sorption process. The series suggests that in the case of propane and butane an identical step is involved, such as hydrogen abstraction from the CH_2 group rather than from the primary carbon atom, as in the case of C_2H_6. For isobutane a tertiary carbon atom with its more loosely bound hydrogen atom may be responsible for the marked decrease in the measured activation energy.

The relative rate of heterogeneous oxidation of the various alkanes appears to run parallel to that of homogeneous, gas-phase oxidation (*14*). However it is most unlikely that we are dealing with a heterogeneously initiated gas-phase oxidation at the temperatures of our catalytic studies. Such hetero-homogeneous reactions have been reported (*4*) at catalyst temperatures much higher than encountered in our measurements. The absence of any stable intermediate oxidation products is indicative of the fact that under our experimental conditions the entire process occurs on the surface of the catalyst. Mass spectrometer analysis of the effluent stream from the reaction vessel indicated the formation of carbon dioxide as the only carbon-containing product following the attainment of the critical reaction temperature. These observations are in agreement with those reported for the Pt-catalyzed oxidation of propane (*8*), and of higher alkanes (*15*), as well as olefins (*2*).

On the basis of the data presented in Table 3 one finds for a given set of experimental conditions a hydrocarbon reactivity sequence as follows:

$$\text{ethane} < \text{propane} \simeq \text{isobutane} < n\text{-butane}$$

This sequence is identical to that encountered in exchange reactions of alkanes with deuterium catalyzed by Pt (*16*). It suggests a similar rate-determining step in catalytic exchange and oxidation of alkanes, namely, dissociative chemisorption of the hydrocarbon molecule with rupture of the same carbon–hydrogen bond.

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