JOURNAL OF CATALYSIS 21, 199-207 (1971)

Catalytic Oxidation Studies with Platinum and Palladium*

ANINA SCHWARTZ, LARRY L. HOLBROOK, AND HENRY WISE

Solid State Catalysis Laboratory, Stanford Research Institute,
Menlo Park, California 94025

Received August 7, 1970

This study of the platinum- and palladium-catalyzed oxidation of selected organic compounds includes aliphatic alkanes, alkenes, alcohols, and ketones. The relationship between chemical structure of reactants and the kinetic parameters of the catalytic reaction (activation entropy and activation energy) is elucidated by these measurements. Fractional surface coverage of the catalyst with chemisorbed oxygen and hydrogen abstraction from the organic compound appear to control the rates of catalytic oxidation. In the alkane series the activation energy diminishes to a constant value at butane. But the observed variations in activation entropy point to electron promotion from the adsorbate to a localized band of the solid as an important aspect of bond formation. Palladium is a less efficient oxidation catalyst than platinum primarily because of the stable oxide (PdO) formed, which exhibits catalytic properties of a metal-oxide semiconductor rather than those of a metal. In the oxidation of 2-propanol over platinum, the formation of acetone at a catalyst temperature near 385°K was observed.

INTRODUCTION

Although considerable attention has been paid to the properties of different catalysts for a given reaction, less information is available on the reaction kinetics and mechanism involving reactants with different functional groups exposed to the same catalyst. In a previous publication (*1*), we reported on the platinum-catalyzed oxidation of several alkanes. The present work extends these studies to several homologous series of organic compounds. In addition, the properties of palladium are compared with those of platinum during catalytic oxidation.

The principle of the experimental technique is the measurement of the catalyst temperature T^* at which transition occurs from a region of kinetic control to one of diffusive control during the course of exothermic catalytic reaction associated with the oxidation process. This approach has been developed theoretically by Frank-Kamenetskii (*2*) in terms of "thermal ignition." Since the experimental method employed by us involves variation of the catalyst temperature rather than reactant concentration, as examined by Frank-Kamenetskii (*2*), we shall present a brief theoretical analysis of the experiment.

THEORETICAL ANALYSIS

Our model considers the energy fluxes resulting from heat generation by exothermic reaction and heat loss by conduction-convection at the catalytic surface immersed in a flowing gas stream containing the reactants and an inert gas. For a given concentration of reactants, the heat generation curve as a function of catalyst temperature exhibits the typical sigmoid shape (Fig. 1), while the heat loss curve is given by a line, such as line *a* (Fig. 1). These two curves intersect at three points, T_{K1}, T_{U1}, and T_{D1}. The temperature T_{K1} cor-

---

* This study was carried out under the sponsorship of a group of industrial companies whose support is gratefully acknowledged.

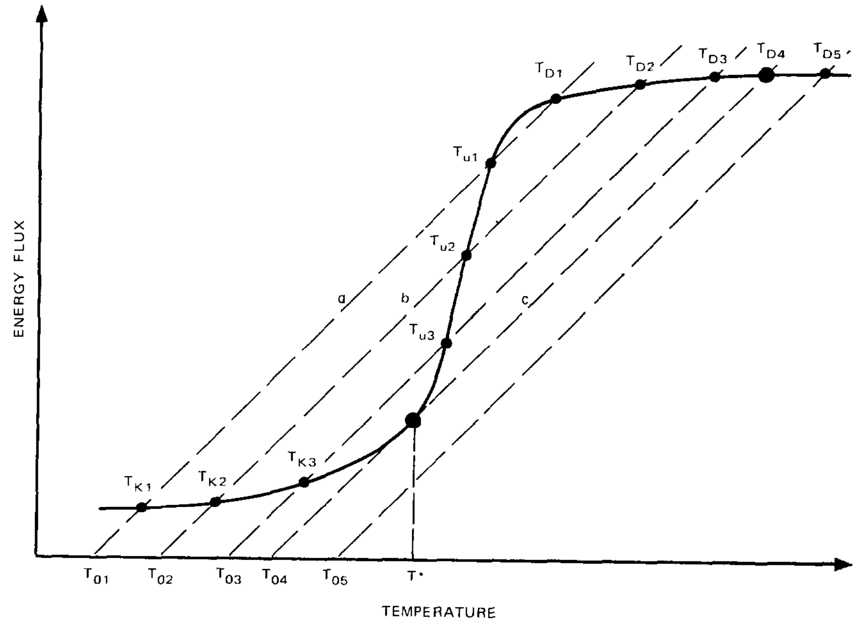

FIG. 1. Schematic presentation of heat-generation flux (solid curve) and heat-loss flux (dashed lines) at different initial catalyst temperatures.

responds to the steady-state condition associated with the region of kinetic-controlled surface reaction, and T_{D1} to the condition of diffusion-controlled surface reaction. The point T_{U1} represents an unstable condition in the transition from kinetic to diffusive control (*2*).

An increase in the catalyst temperature due to external heating (as done in our experiments) causes a shift in the heat loss curve from *a* to *b* (Fig. 1) without change in slope since the heat transfer coefficient remains constant. Thus, in the absence of chemical surface reaction, the gas temperature in contact with the catalyst has been raised from T_{01} to T_{02} and, in the presence of reactants, the kinetic-controlled steady-state temperature is shifted from T_{K1} to T_{K2}. For every initial catalyst temperature, the system will attain a steady-state temperature T_{Km} $(m = 1, 2, 3 \ldots)$, where $T_{Km} > T_{0m}$ since in this region the heat generation curve falls below the heat loss curve. However, when the system attains the condition specified by line *c* (Fig. 1), the heat loss curve and the heat generation curve no longer intersect but they are tangent to each other at T^*. The kinetic-controlled regime no longer provides a steady-state condition and the system now exhibits the phenomenon of "ignition," i.e., a rapid transition to the diffusion-controlled steady-state temperature T_{D4}.

Under steady-state conditions the diffusive flux of reactant to the catalyst is balanced by the rate of surface reaction, so that for a first-order reaction at the catalytic surface

$$-D\left(\frac{dn}{dx}\right) = kn, \tag{1}$$

where n is the reactant concentration in close proximity to the catalytic surface, D the multicomponent diffusion coefficient, k the chemical rate constant, and x a distance coordinate. For the case of a single reactive species present at low concentrations and undergoing heterogeneous reaction, the following one-dimensional steady-state equation offers a satisfactory approximation

$$\frac{d^2n}{dx^2} = 0. \tag{2}$$

The boundary conditions applicable to this system read:

$$n = n_0 \text{ at } x = 0 \text{ (in gas)},$$
$$n = n \text{ at } x = L \text{ (at catalyst)},$$

where L represents the distance from the source to the catalyst surface.* Integration of Eq. (2) yields

$$\frac{n}{n_0} = 1 + \frac{a}{n_0}\frac{x}{L}, \tag{3}$$

which reduces to $n/n_0 = 1 + (a/n_0)$ at $x = L$, where a is a constant of integration.

One obtains by differentiation of Eq. (3):

$$\frac{dn}{dx} = a/L, \tag{4}$$

which on substitution from Eqs. (1) and (3) leads to the following expression at $x = L$:

$$\frac{-Da}{L} = kn_0\left(1 + \frac{a}{n_0}\right). \tag{5}$$

The integration constant is found to be

$$a = -\frac{kn_0}{[k + (D/L)]}. \tag{6}$$

Thus from Eq. (4) $dn/dx = -kn_0/(D + kL)$, so that

$$-D\left(\frac{dn}{dx}\right) = \frac{kn_0}{[1 + (kL/D)]}. \tag{7}$$

For the conditions prevailing in the kinetic-controlled region $kL/D \ll 1$ and

$$-D\left(\frac{dn}{dx}\right) = kn_0 = F_K \tag{8}$$

where F_K represents the mass flux at the catalyst surface.

In the diffusion-controlled region $kL/D \gg 1$ so that the mass flux F_D is given by

$$F_D = -D\left(\frac{dn}{dx}\right) = D\left(\frac{n_0}{L}\right). \tag{9}$$

This result may be generalized to surface reactions of order y if the concentration of reactant in the bulk stream remains essentially constant up to the catalytic surface; that is, small mass gradients are experienced near the catalyst–gas interface because of kinetic limitations. We conclude that to a first approximation based on Eq. (8) the mass flux of reactant at the catalytic surface is equal to

$$F_K \simeq kn_0^y. \tag{10}$$

The energy balance for the system requires that at steady state the heat flux due to chemical reaction must be equal to the heat loss by convective and conductive heat transfer. Thus in the kinetic-controlled regime

$$Qkn_0^y = \alpha(T - T_0)_m, \tag{11}$$

where Q is the heat of reaction, and α the heat transfer coefficient. The term T_{0m} represents the parameter that is varied in our experiment by heating of the catalyst from an external energy source. Since the rate constant is a function of temperature as given by the Arrhenius expression, one obtains from Eq. (11)

$$Qn_0^y z e^{-E/RT} = \alpha(T - T_0)_m, \tag{12}$$

where E is the activation energy, and z the preexponential coefficient. At $T = T^*$:

$$Qn_0^y z e^{-E/RT^*} = \alpha(T^* - T_0)_m,$$

and the curves are tangent to each other so that the derivatives with respect to T^* are equal. Therefore,

$$\frac{\alpha}{Qn_0^y z} = \frac{E}{R(T^*)^2} e^{-E/RT^*}. \tag{13}$$

The kinetic parameters of interest (y, z, E) may be evaluated by the following experimental measurements: (1) at constant reactant concentration n_0 the value of T^* is examined as a function of α (to this end the flow rate over the catalyst surface may be varied, thereby changing the heat transfer coefficient), and (2) at constant α, the value of T^* is determined over a range of reactant concentrations. The first series of experiments yields the value of the activation energy E, while the second series allows evaluation of the reaction order y. Finally, the preexponential coefficient z may be obtained by direct substitution of the derived quantities in Eq. (13).

---

* In more complex reactor configurations L is a characteristic linear dimension of the system.

EXPERIMENTAL DETAILS

The apparatus employed was of the same type as described in Ref. *1*. Since liquid materials were employed in some of the measurements a special vaporizer was assembled for the introduction of known concentrations of vapor of the desired organic compound into the carrier gas stream (N_2) to which oxygen was added subsequently. A special feed mechanism was constructed to displace the liquid at an adjustable rate from a syringe into the vaporizer (Fig. 2). The vaporizer was composed of a 12-W enameled resistor covered with several layers of Fiberglass thread into which the syringe needle was buried. The temperature of the resistor was adjusted by an external electrical power supply to a level that would ensure complete vaporization of the liquid. The vapor was carried away in an inert gas stream (N_2) whose flow rate was metered. The concentration of reactant in the gas stream was controlled by adjusting the rate of advance of the motor-driven piston in the syringe containing the liquid. The vaporizer assembly was contained in a glass cylinder connected through a constriction to another chamber where metered quantities of oxygen were added to the gas mixture. The constriction between the two chambers prevented back diffusion of oxygen into the vaporizer. The gas containing the vaporized reactant, nitrogen, and oxygen then entered a mixing chamber packed with glass capillary tubing. An aliquot of the sample flowed over the catalyst, while the remainder was discharged into the atmosphere.

The metal filaments used as catalysts were coiled into a helix and positioned in the reactor normal to the direction of gas flow. Two filaments were employed, one of which was exposed to the flowing gas stream containing the organic material, oxygen, and nitrogen, while the other came in contact only with an oxygen–nitrogen mixture ($O_2 = 20$–40 vol %). These filaments were part of a Wheatstone bridge circuit excited by direct current from a regulated variable power supply. Both the bridge output signal, related to net heat release, and the current through the filaments, proportional to their temperature, were monitored and displayed on an x–y recorder. As the filament temperature was gradually raised by joule heating, the system attained the critical temperature T^*, at which point an abrupt change in bridge output voltage was discerned (Fig. 3). By empirical calibration of the filament resistance as a function of filament current, the signal associated with "ignition" could be translated into the temperature of the active catalyst filament T^*.

To evaluate the kinetic parameters, the ignition temperature was determined as a function of reactant concentration (<2 vol %) at several total gas flow rates. The heat transfer coefficient from the filament

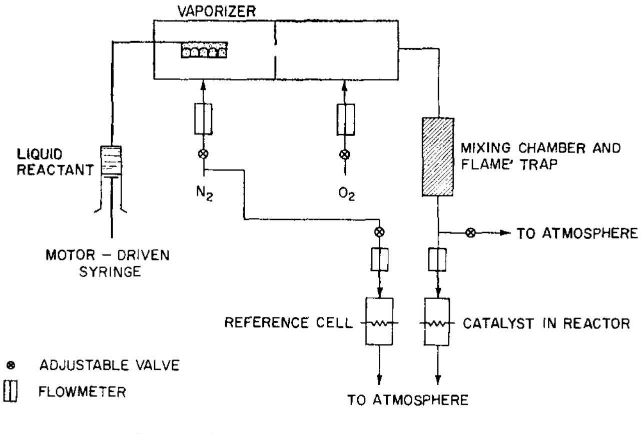

FIG. 2. Schematic diagram of apparatus.

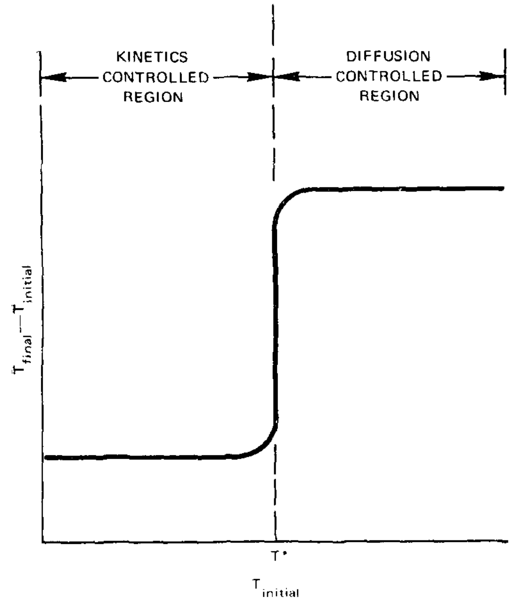

FIG. 3. Catalyst temperature during transition from kinetics control to diffusion control.

to the moving gas stream was determined experimentally by measuring the energy required to maintain the filament temperature at different values. The results of these measurements are shown in Table 1. Since the concentration of organic reactant was kept at less than 2 vol % of the total gas mixture, it had no measurable influence on the thermal conductivity of the gas mixture. The purity and source of the materials employed in our studies are shown in Table 1.

EXPERIMENTAL RESULTS

For the catalytic oxidation studies we selected a group of organic compounds that would allow us to draw some conclusions concerning the role of chemical structure in chemical reactivity. Presently the organic materials comprise alkanes, olefins, alcohols, and ketones. In each of the cases cited, the order of the reaction with respect to the organic compound was determined under our experimental conditions. It will be recalled that the concentrations of organic reactant were kept low (2 vol %) with excess oxygen in the carrier stream. As a result our experiments shed no light on the reaction order with respect to oxygen.

Platinum

The data shown in Table 3 summarize the results obtained with Pt as a catalyst for the oxidation of alkanes, alcohols, and ketones. For the compounds listed the oxidation exhibited first-order kinetics and led to CO_2 and/or CO and water as the reaction products, as determined from samples withdrawn for analysis by mass spectrometry and gas chromatography. With 2-propanol a stable intermediate product was noted as evidenced by the appearance of two consecutive "run-away" exothermic reactions with increasing catalyst temperature (Fig. 4). At a catalyst temperature near 385°K the formation of acetone could be detected. The mole fraction of acetone

TABLE 1
PHYSICAL PROPERTIES OF CATALAYSTS

Catalyst	Length (in.)	Diameter		T coeff. resistivity $\times 10^3$	Heat transfer data	
		Filament (in.)	Helix (in.)		Gas flow rate (cm^3 min^{-1})	Coefficient (cal cm^{-2} sec^{-1} deg^{-1}) $\times 10^3$
Pd[a]	2.04	0.003	0.054	3.28	100	5.00
Pd[a]	3.05	0.003	0.054	3.28	100	4.23
Pt[b]	2.97	0.003	0.054	3.92	50	1.32
					135	1.62
					400	2.44

[a] Manufactured by Johnson-Matthey & Co., Ltd.; purity, 99.99 wt %.

[b] Manufactured by Wesgo; purity, 99.99 wt %.

TABLE 2
MATERIALS USED IN EXPERIMENTAL MEASUREMENTS

Material	Source	Purity (vol %)
Ethane	Matheson	99 M
n-Propane	Matheson	99 M
n-Butane	Matheson	99 M
Isobutane	Matheson	99 M
n-Octane	Phillips 66	99 M
2,2,4-Trimethylpentane	Phillips 66	99.98
2,3,4-Trimethylpentane	Phillips 66	99.52
Cyclohexane	Matheson Coleman & Bell	Pract.
Methanol	Mallinckrodt	99.5
Ethanol	Commercial Solvents Corp.	95
1-Propanol	Mallinckrodt	99.5
2-Propanol	Mallinckrodt	99.5
Acetone	Allied Chemical	99.5
Methyl ethyl ketone	Shell Chemical Corp.	99.5
3-Pentanone	Eastman Organic Chemicals	Pract.

formed appeared to be a function of the partial pressure of oxygen in the gas stream (Table 4). A comparison of the rate constant for complete oxidation of acetone with that for acetone formation from 2-propanol yields a ratio of 0.02 at 500°K. Therefore, in the temperature region encountered in our studies the isolation of acetone as a stable intermediate oxidation compound is to be expected.

The Pt-catalyzed oxidation of the olefins exhibited more complex behavior than observed for the alkanes. The reaction was found to be of inverse fractional order with respect to the olefin, as noted also by Patterson and Kemball in an earlier study of propylene oxidation (*4*) by an entirely different experimental method. This effect manifested itself in our measurement by

TABLE 3
KINETIC DATA ON CATALYTIC OXIDATION ON PLATINUM

Compound	*E* (kcal/mole)	$\log_{10} z$
Ethane	27.3[a]	7.45[a]
Propane	17.6[a]	9.04[a]
Butane	17.0[a]	9.52[a]
Isobutane	10.2[a]	5.66[a]
Octane	17.6	7.78
2,2,4-Trimethylpentane	13.9	7.78
2,3,4-Trimethylpentane	13.7	7.33
Methanol	13.4	9.92
Ethanol	13.2	9.66
1-Propanol	13.2	8.95
2-Propanol	8.2	4.77
2-Propanol	12.8[b]	8.73[b]
Acetone	15.7	8.52
Methyl ethyl ketone	14.8	9.56
Diethyl ketone	14.7	8.98

[a] Values taken from Ref. *1*.

[b] Partial oxidation to acetone in gas mixture containing 40 vol % O_2.

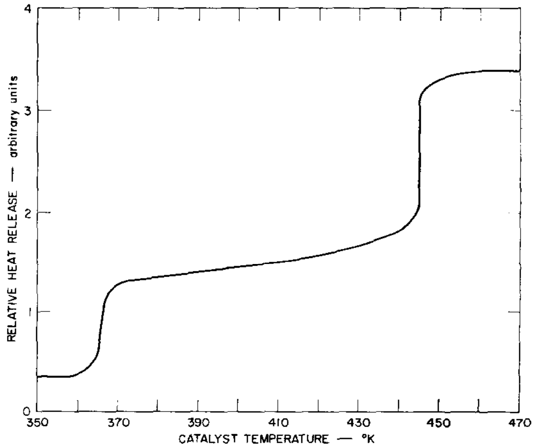

FIG. 4. Oxidation rate of isopropyl alcohol as a function of catalyst temperature (Gas composition (vol %): $i\text{-}C_3H_7OH = 2.3$, $O_2 = 40.0$, $N_2 = 57.7$; $P_{tot} = 1$ atm).

TABLE 4
CATALYTIC OXIDATION OF 2-PROPANOL TO ACETONE ON PLATINUM

Oxygen (vol %)	Acetone (relative units)[a]
9.5	0.6
19	0.7
40	1.0

[a] The acetone yield at 40 vol % O_2 is taken as unity.

an increase in the transition temperature with rising olefin concentration. The results of these determinations are shown in Table 5.

TABLE 5
OXIDATION OF OLEFINS CATALYZED BY PLATINUM

Compound	E (kcal/mole)	$\log_{10} z$[a]	Reaction order (y)
C_3H_6	22.0 ± 0.7	1.29	−0.25
C_4H_8	16.6 ± 2.4	2.98	−0.2

[a] Units of pre-exponential factor z are $(cm^3)^{y-2}$ $sec^{-1}mole^{1-y}$.

Palladium

Although the Pd-catalyzed oxidation studies do not include as great a number of organic compounds as for Pt, the results obtained (Table 6) are useful in suggesting the marked differences in catalytic behavior between these two metals. Of interest is the observed first-order, kinetic dependency of the compounds studied, including the olefins. This marked difference in reaction order of the olefins during oxidation over Pd and Pt has previously been reported (*5*) (Table 7).

TABLE 6
CATALYTIC OXIDATION OF ORGANIC COMPOUNDS OVER PALLADIUM

Compound	Transition temp T^*(°K)[a]	Activation energy E (kcal/mole)	Preexponential factor $\log_{10} z$[b]
C_3H_8	598	24.4	10.81
n-C_8H_{18}	457	26.0	14.51
2,2,4-Trimethyl pentane	505	39.4	19.58
C_2H_4[c]	559	10.3	7.04
C_2H_4[d]	514	15.8	10.05
C_3H_6	502	24.8	11.10
Cyclo-C_6H_{10}	396	33.8	20.38
CH_3OH	445	36.4	22.38
i-C_3H_7OH	564	28.4	13.60

[a] Transition temperature from kinetic- to diffusion-controlled region for reactant concentration of 1.35×10^{-7} mole/cc.
[b] Units of preexponential factor z are cm·sec^{-1}.
[c] Oxygen = 10 vol %.
[d] Oxygen = 40 vol %.

DISCUSSION

The results of our experiments with Pt (Table 3) give some insight into the relationship between the structure of the organic molecule and the rate of its catalytic oxidation. In the homologous series of n-alkanes the differences in the activation energies appear to be related to the C–H bond strengths present in the molecule, a fact which points to hydrogen abstraction as a primary process. Of interest is the observation that the activation energy attains a constant value for propane and higher alkanes. It may be concluded that in the oxidation mechanisms of these com-

TABLE 7
OXIDATION OF OLEFINS CATALYZED BY PALLADIUM AND PLATINUM

Catalyst	Olefin	Activation energy (kcal/mole)		Reaction order	
		Present work	Literature	Present work	Literature
Pd	C_2H_4	15.8	14.3 ± 0.6[a]	1	1[a]
Pd	C_3H_6	24.8	20.8 ± 1.3[b]	1	1[b]
Pt	C_3H_6	22.0	17.0 ± 0.7[b]	−0.25	−0.2[b]

[a] KEMBALL, C., AND PATTERSON, W. R., *Proc. Roy. Soc. Ser. A* **270,** 219 (1962).
[b] PATTERSON, W. R., AND KEMBALL, C., *J. Catal.* **2,** 465 (1963).

pounds an identical step is involved, viz., hydrogen abstraction from a secondary carbon atom which energetically is less expensive than abstraction from a primary carbon atom as in ethane. The total number of secondary carbon atoms in a given molecule appears to be of little consequence. In line with this conclusion is the marked decrease in activation energy on the introduction of a tertiary carbon atom as in isobutane and the substituted octane isomers (Table 3). Again the total number of tertiary carbon atoms in a molecule has no effect on the activation energy. Thus the process of oxidation appears to be initiated with dissociative chemisorption during which the weakest C–H bond is broken. Since the number of primary, secondary, or tertiary carbon atoms does not influence the activation energy, the formation of such a radical with the loss of a single hydrogen is adequate to initiate the oxidation process by oxygen chemisorbed on neighboring metal sites. The catalytic properties for complete oxidation appear to be most favorable when the metal surface has the ability to maintain fractional surface coverage with both reactants, viz., hydrocarbon and oxygen, a condition which may be the major cause for the observed difference in the catalytic properties of Pt and Pd (vide infra). Recent experimental measurements indicate that during oxygen adsorption the ratio of Pt/O approaches the value of two on the surface of a platinum ribbon (6–8).

In the case of the ketones the differences in activation energies are small for the limited number of compounds studied. The presence of the C=O group appears to conceal the role played by primary and secondary carbon atoms which is so prominent in alkane oxidation.

The results for the alcohols show a pattern similar to that of the alkanes. Again the initial attack occurs at the weakest C–H bond (e.g., 1-propanol vs 2-propanol) with some effect caused by the presence of the hydroxyl group. The variation in reactivity of the alcohols appears to be due entirely to the preexponential factor. At 500°K the differences in the rate constants are appreciable when one compares the C_1 through C_3 series (Table 8). These differences in activation entropy for the oxidation of various compounds may be related to electron promotion from the adsorbate to a localized band of the solid (*9*). The activation entropy changes must be inherent to the structure of the reactant, and the surface-state energy level it occupies relative to the Fermi level of the solid. Such a concept of electronic charge transfer has been applied also to metal-catalyzed hydrogenation of olefins (*10*).

For the organic compounds investigated in this study, the reactivity pattern observed in the case of Pt does not emerge as clearly in the case of Pd, although we are inclined to believe that hydrogen abstraction continues to play an important role.

TABLE 8

PT-CATALYZED OXIDATION OF ALCOHOLS

Compound	Rate constant at 500°K (cm/sec)
Methanol	1.2×10^4
Ethanol	7.5×10^3
1-Propanol	1.4×10^3
2-Propanol	1.5×10^1

In the olefin series the results of our measurements may be compared with the data obtained by other workers employing evaporated films (Table 7). Our values for the activation energies are somewhat higher than those reported in the literature. For the olefin oxidation over Pd, a first-order reaction was reported for evaporated films as suggested also by our measurements. In the case of Pt the negative reaction order reported was confirmed in our measurements.

In Table 6 we present two activation energy values for C_2H_4 oxidation. At low oxygen concentrations (<10%) we observed partial oxidation of C_2H_4, which may represent the formation of acetaldehyde and/or acetic anhydride as noted by Kemball and Patterson (*5*). The latter compound has been found to be resistant to further oxidation over a Pd-catalyst and to inhibit C_2H_4 oxidation (*5*).

The observed differences between the catalytic properties of Pd and Pt are most likely associated with variations in the degree of oxygen coverage exhibited by these two metals. For Pd, sorption data (*8*) and thermodynamic studies (*11*) indicate the existence of both a strongly bound oxygen adsorbate with high surface coverage and a metal-oxide compound at the partial pressures of oxygen employed in our measurements. In the studies with Pt we suggest the coexistence of chemisorbed organic reactants and oxygen on neighboring sites as an essential requirement for complete oxidation. Such a condition appears to be more difficult to attain in the case of Pd because of its tendency to form a stable metal-oxide surface layer at the temperatures studied. As a matter of fact, we noted in our work that a visible oxide layer formed by prolonged exposure of the Pd-filament at elevated temperatures to the oxygen-containing gas stream in the absence of organic reactants. Such pretreatment caused loss of metallic appearance of the catalyst and complete inhibition of the catalytic oxidation, especially in the case of the alkanes, while it had no deleterious effect with olefins or alcohols. The oxide layer could be removed at a measurable rate by exposure of the catalyst to CO at elevated temperature ($T >$ 500°K). However, admixture of CO (0.3 vol %) to the reactant stream during Pd-catalyzed oxidation of the organic compounds studied led to higher values of T^* than in the absence of CO. This interference by CO may be responsible for the apparent inhibition in reaction rate noted in the oxidation of methanol at high concentrations (<3 vol %). This alcohol is known to decompose to CO and H_2 over a Pt[12] or Ni[13] catalyst in the absence of oxygen, and to retard the reaction rate. Most likely it yields CO as an oxidation product in our experiments, since some preliminary measurements of CO-oxidation over Pd by our experimental technique have indicated that the reaction order with respect to CO is less than zero, i.e., CO acts as an inhibitor.

REFERENCES

1. HIAM, L., WISE, H., AND CHAIKEN, S., *J. Catal.* **10**, 272 (1968).
2. FRANK-KAMENETSKII, D. A., "Diffusion and Heat Exchange in Chemical Kinetics" (N. Thon, transl.). Princeton Univ. Press, Princeton, N. J. 1955.
3. WISE, H., AND WOOD, B. J., *in* "Advances in Atomic and Molecular Physics" (D. R. Bates and I. Estermann, eds.), Vol. 3, pp. 291–353. Academic Press, New York, 1967.
4. PATTERSON, W. R., AND KEMBALL, C., *J. Catal.* **2**, 465 (1963).
5. KEMBALL, C., AND PATTERSON, W. R., *Proc. Roy. Soc. Ser. A* **270**, 219 (1962).
6. VANSELOW, R., AND SCHMIDT, W. A., *Z. Naturforsch. A* **22**, 717 (1967); **21**, 1690 (1966).
7. TUCKER, C. W., *J. Appl. Phys.* **35**, 1897 (1964).
8. BRENNAN, D., HAYWARD, D. O., AND TRAPNELL, B. M. W., *Proc. Roy. Soc. Ser. A* **256**, 81 (1960).
9. WISE, H., *J. Catal.* **10**, 69 (1968).
10. TURKEVICH, J., NOZCKI, F., AND STAMIRES, D., *"Third Congress on Catalysis"* (W. M. Sachtler *et al.*, eds.), p. 586. Wiley, New York, 1965.
11. BELL, W. E., INYARD, R. E., AND TAGAMI, M., *J. Phys. Chem.* **70**, 3735 (1966).
12. MCKEE, D. W., *Trans. Faraday Soc.* **64**, 2200 (1968).
13. YASUMORI, I., NAKAMURA, T., AND MIYAZAKI, E., *Bull. Chem. Soc. Jap.* **40**, 1372 (1967).