JOURNAL OF CATALYSIS 16, 220–231 (1970)

Catalytic Oxidation

II. Silica Supported Noble Metals for the Oxidation of Ethylene and Propylene

NOEL W. CANT AND W. KEITH HALL

Carnegie-Mellon University, Mellon Institute, Pittsburgh, Pennsylvania 15213

Received May 28, 1969; revised July 15, 1969

The catalytic oxidation of C_2H_4 and C_3H_6 was studied over silica-supported Pt, Pd, Ir, Ru, and Rh. The specific activities fell in the order listed and correlated with the percentage *d*-character of the metal and fairly well with its atomic radius. The partial oxidation products were characterized. Acetaldehyde and acetic acid were produced from C_2H_4 in all cases, but only with Pd and Ir were the quantities significant. Products from C_3H_6 were more varied. C_3 products in substantial amounts were formed over Rh, Ru, and Pd, the selectivity decreasing in the order given. Somewhat smaller amounts of C_2 products were also formed over these catalysts. The principal product over Ir was acetic acid; the most active catalyst, Pt, was relatively unselective. Three different types of pressure dependencies were found: the rate of total oxidation decreased with olefin pressure and increased with oxygen pressure over Pt and Pd; the rate increased with olefin pressure and was inhibited by oxygen over Rh and Ir; and the rate increased with oxygen pressure, but was nearly independent of olefin pressure over Ru. Activation energies varied from 16 to 29 kcal/mole and tended to correlate inversely with the catalytic activity. The order of activity depended upon the ability of the metal to activate O_2.

INTRODUCTION

Work on the oxidation of ethylene and propylene over noble metals has been summarized in several recent reviews (*1–3*). Ethylene oxidation over silver catalysts has been investigated extensively because of the commercial importance of ethylene oxide, but much less study has been devoted to the other noble metals, where the chief products tend to be CO_2 and H_2O. Thus, Reyerson and Swearingen (*4*) reported that C_2H_4 oxidation over Pd supported on silica gel yielded only CO_2 and H_2O. Butyagin and co-workers (*5, 6*) obtained similar results for C_3H_6 over Pt on $BaCO_3$, and Morooka and Ozaki (*7*) did not detect any partial oxidation products when C_3H_6 was oxidized over Pt or Pd supported on SiC. However, Kemball and Patterson (*8*) oxidized C_2H_4 over an evaporated Pd film in a static reactor and found that about 3% of the product appeared as acetic anhydride and acetic acid. Since they found acetaldehyde oxidized rapidly to acetic anhydride under their reaction conditions, they suggested that it might be a short-lived intermediate, although it was not detected. In a later, more extensive investigation, these workers (*9*) did not find acetic anhydride when C_2H_4 was oxidized over Pt or Rh but acetone, in amounts not exceeding 8%, was formed when C_3H_6 was oxidized over Pt, Pd, or Rh.

In a recent communication from this laboratory (*10*), it was shown that the selectivity of Pd for C_2H_4 oxidation to acetic anhydride and acetic acid could be raised to 20–30% by carrying out the reaction at low conversion in a recirculating differential reactor, using product removal after each pass over the catalyst. With this system, trace amounts of acetaldehyde were positively identified. Alloying Pd with

Au produced substantial changes in the selectivity to partial oxidation products; a maximum selectivity of 70% was achieved for the composition containing 20% Pd. These studies have been extended in the present work to include all of the noble Group VIII metals except Os, which was excluded because of its tendency to form the volatile, toxic OsO_4. C_3H_6, as well as C_2H_4, was oxidized and the products were characterized. The gross kinetics of both reactions were determined. These results, which are of interest in themselves, form the foundation for tracer experiments to be reported later.

Experimental Methods

Equipment

The kinetic studies were carried out in the single-pass flow reactor shown diagrammatically in Fig. 1. Approximately 2 cm³ of catalyst, sieved to 20–30 mesh, were loaded into a tubular Pyrex reactor which had a thermocouple well imbedded in the center of the reaction zone. The inlet and outlet of the reactor were connected to a six-port, two-position stainless steel valve. In one position, either hydrogen or helium could be flowed over the catalyst for pretreatment purposes, while in the other, the reactant stream of olefin (3–80 Torr), oxygen (10–150 Torr), and helium (to a total pressure of 1 atm) was turned over the catalyst. The total flow rate was maintained constant in the range 40–50 ml (STP) min⁻¹ in all experiments. The products passed through an eight-port, two-position valve and its 5 cm³ sample loop (approx. 50 cm of thin walled ⅛-in. diam. stainless steel tubing) to the vent. With this valve in its alternate position, the stream flowed directly to the vent while, simultaneously, the contents of the sampling loop were swept through a column switching valve to either of two gas chromatographic columns. The three switching valves were contained within an insulated enclosure heated to 100° to prevent condensation of the partially oxygenated products. The two columns and their thermal conductivity detectors were thermostated in separately heated ovens.

Techniques

The complete oxidation of olefins is an extremely exothermic reaction (~330 kcal mole⁻¹ for ethylene). In the present experiments, the apparent rise in catalyst temperature due to the heat of reaction was kept below 3° by running the reactions at low olefin conversions (<40%, maximum oxidation rate <0.3 ml (STP) min⁻¹) in the He diluent.

In order to collect sufficient amounts of partial oxidation products for identifica-

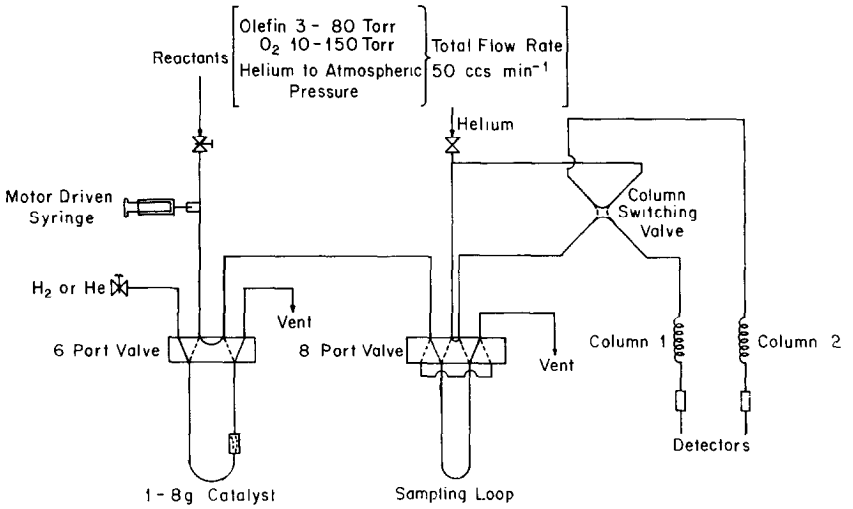

FIG. 1. Schematic diagram of flow reactor system.

tion, it was customary to cool the sampling loop to −78° and to accumulate the condensable products for a fixed time interval. (−195° was used for analyses of CH_3CHO and CH_2CHCHO.) Blank experiments showed that this collection procedure was >98% efficient. The pressures of the noncondensable components (O_2, CO_2, and olefin) were determined by sending the gas phase in the loop to one column. The condensed products were separated and the amount of each was determined using the second column. Both columns were packed with porous polymer beads (Porapak Q or R, Waters Associates, Inc.). The first column was 6 ft of 0.25-in. tubing thermostated at about 75°; the second was 5 ft of 0.25-in. tubing thermostated at 165°. All reactants and products were determinable in this manner. Identification of the partial oxidation products was based upon a comparison of retention times with those of authentic samples and on mass spectra determined from samples collected as they were eluted from the columns.

Reagents

The ethylene was either Lif-o-gen Research Grade or Matheson CP grade; propylene was Matheson CP grade. Both olefins were used without purification since the only detectable impurities were air, and a small amount (<0.1%) of the corresponding paraffins. Oxygen (Linde USP) was also used as supplied, but the hydrogen (Airco 99.9%) and helium (Airco 99.995%) were passed through a trap containing activated charcoal cooled to −196°C.

Catalysts

The silica-supported noble metal catalysts were prepared following the method of Sinfelt and Yates (*11*). The silica was Cabosil HS-5 (surface area, 330 m^2/g); it was impregnated with aqueous solutions of noble metal salts of such strength that the final metal content was about 5%. The use of halide or sulfate-containing salts was avoided, except as noted, because these ions could modify the selectivity and activity of metals. The metal salts employed were $Pd(NO_3)_2$, $Ru(NO_3)_3$ (10% solutions), and $Pt(NH_3)_2(NO_2)_2$ (Englehard Industries), and $Rh(NO_3)_3$ and H_2IrCl_6 (Alfa Inorganics). Each salt was stated to have been prepared from the corresponding metals of not less than 99.9% purity.

Prior to use as a catalyst, each preparation was pretreated in a standard way. This consisted of flowing hydrogen at 50 ml min^{-1} over the material while the temperature was raised to 300° over a 2-hr period. The reduction was continued at 300° for a further 3–6 hr following which the system was purged with helium overnight. These relatively mild conditions were employed to minimize the uptake of product water by the support during the initial stages of the reaction. The experiments of Newkirk and McKee (*12*) indicate that reduction was almost certainly complete under our conditions.

The metal surface area of each catalyst was determined as described by Sinfelt and Yates (*11*) with an aliquot of each batch given the same reduction and evacuation pretreatment. The samples were protected from mercury vapor during evacuation and subsequent hydrogen or carbon monoxide adsorption by a liquid nitrogen trap.

Treatment of Data

CO_2 and H_2O were the chief reaction products. Partial oxidation products which formed in detectable amounts included acetic acid and acetaldehyde from ethylene and acrolein, acetone, acetic acid, acetaldehyde, and small quantities of acrylic and/or propionic acid from propylene. The following overall stoichiometric equations were assumed:

$$C_3H_6 + \tfrac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O, \quad (1)$$

$$C_3H_6 + O_2 \rightarrow CH_2CHCHO + H_2O, \quad (2)$$

$$C_3H_6 + \tfrac{1}{2}O_2 \rightarrow CH_3COCH_3, \quad (3)$$

$$C_3H_6 + \tfrac{5}{2}O_2 \rightarrow CH_3COOH + H_2O + CO_2, \quad (4)$$

$$C_3H_6 + 2O_2 \rightarrow CH_3CHO + CO_2 + H_2O. \quad (5)$$

The selectivity to any one product was defined as the percentage of all of the propylene oxidized which was converted (according to one of the above equations) to

this product. The overall rates of formation of H_2O and partial oxidation products were determined directly (μM min^{-1}) from the amounts of these collected per unit time in the sampling loop, and the selectivities were calculated from these data as this was the most accurate method. However, the rate of CO_2 formation was calculated from its measured pressure in the gas stream, knowing the total gas flow rate. This provided a check on the rate of total oxidation since the rates of carbon dioxide and water formation could be compared on the basis of values expected according to Eqs. (1–5). In general, the agreement was within the overall experimental error of $\pm 5\%$ at low conversions.

The apparent activation energies and pre-exponential factors for the overall oxidation rates were calculated from the variation of rate with temperature using a least squares analysis with the Arrhenius equation. The same computer program gave the standard deviation in both E_a and A and was also used to calculate the rate and its standard deviation at the temperature at which it was desired to compare catalyst activities. Since the metal surface areas had been measured, it was possible to convert the calculated rates to specific rates (units of molecules sec^{-1} cm^{-2}). These data were corrected to the *standard* pressures chosen for comparison (olefin pressure, 20 Torr; oxygen pressure, 65 Torr), using experimentally determined pressure dependencies. In general, this correction was small ($<20\%$) since conditions were used which approximated those chosen for comparison.

Results

When the catalysts were first exposed to the stream of reactants, the temperature rose rapidly by as much as 15°. This probably corresponded to both the heat of adsorption of reactants and to the heat of reaction on the most active portions of the metal surface. The catalysts lined out over a period of hours and the temperature and the rates fell to steady values. The maximum conversion usable in the steady state was limited by the temperature rise; above a critical conversion, the heat release led to a runaway reaction with total reactant conversion. These problems were minimized by starting the reaction 50–100° below the desired reaction temperature, and by raising the temperature in steps as the catalyst lined out.

The rhodium catalyst was difficult to work with for another reason as under certain conditions the mechanism appeared to change. At any temperature (including those giving very low reaction rates) critical reactant compositions were found to exist, such that lower O_2 pressures or higher olefin pressures, resulted in total conversion. This suggested a radical chain mechanism although the products observed under these conditions (acetic acid $\leqslant 5\%$ was the sole partial oxidation product) did not correspond to those reported for homogeneous oxidation in a flow system (*13*) (acetaldehyde 34%, propylene oxide 24%, acrolein 12%, allyl alcohol 5%). Hence, the metal played a role. Neither did the oxidation of propylene over any of the other catalysts under non-runaway conditions approximate this distribution.

Tables 1 and 2 list the partial oxidation products formed during ethylene and propylene oxidation, respectively, in the steady state and with the standard reactant pressures. Products stated to have selectivities $>1\%$ were positively identified by mass spectral methods. Ethane, propane, carbon monoxide, formaldehyde, formic acid, allyl alcohol, propylene oxide, or propionaldehyde were not detected in more than trace amounts. The upper limits for the selec-

TABLE 1
Selectivity to Partial Oxidation Products During Ethylene Oxidation over Silica-Supported Metals[a]

Metal	Acetaldehyde	Acetic acid
Ru	<0.1	<0.5
Rh	≤1	≤1
Pd	≤3[b]	15–25
Ir	<0.1	8–13
Pt	0.2	0.8

[a] Data correspond to the standard activity conditions of Table 3.

[b] Includes a small amount of ethylene oxide.

TABLE 2
SELECTIVITY TO PARTIAL OXIDATION PRODUCTS DURING PROPYLENE OXIDATION OVER SILICA-SUPPORTED METALS[a]

Metal	Acetaldehyde	Acetic acid	Acrolein	Acetone	C_3 Acids
Ru	3–9[b]	6–10[b]	5–14[b]	2–7[b]	0.5
Rh	0.5–2.0[c]	2–5	10–25[c]	6–9	<0.5
Pd	<0.2	1.5–3.0	1.0–3.0	2.5–4	0.5
Ir	<0.2	28–32	0.5–1.0[c]	3–4	2–3[d]
Pt	<0.1	<0.4–0.9	0.1	0.2–0.7	<0.5

[a] Data correspond to standard activity conditions of Table 4.
[b] Time dependent, maxima and minima correspond to several- and 50-hr operation, respectively.
[c] Conversion dependent.
[d] Approximately $\frac{2}{3}$ propionic acid.

tivity to these compounds was set at 1% for carbon monoxide, propylene oxide, and propionaldehyde and at 0.1% for ethane, propane, formaldehyde, formic acid, and allyl alcohol.

Ethylene oxidation over palladium sponge (*10*) and evaporated films (*8*) yielded both acetic acid and acetic anhydride. Apparently the latter compound was completely hydrolyzed over the Pd/SiO_2 catalyst, because acetic acid was detected in an amount equivalent to the sum of the two products over the unsupported metal. Similar trace quantities of acetaldehyde were formed over both catalysts. In agreement with the results of Patterson and Kemball (*9*), Rh/SiO_2 and Pt/SiO_2 were less selective than Pd/SiO_2; the former catalysts produced small quantities of both acetic acid and acetaldehyde, however, which they did not observe. Our new findings include the fact that Ru/SiO_2 is equally unselective in ethylene oxidation and that Ir/SiO_2 approaches Pd/SiO_2 in its efficiency for acetic acid formation. Unlike Pd, however, only a trace of acetaldehyde was formed over Ir/SiO_2.

The oxidation of C_3H_6 over the same catalysts led to a much wider variety of products than did C_2H_4. In particular, Ru/SiO_2 yielded a variety of products since, in addition to those listed, the chromatograms indicated at least two other compounds in trace amounts (<0.1%). These were tentatively identified as ethanol and propylene oxide (or propionaldehyde). The selectivities to acrolein, acetone, acetic acid, and acetaldehyde were time dependent over Ru/SiO_2; the maximum and minimum values shown in Table 2 refer to a few hours and 50-hr operation, respectively. Thereafter, the selectivities remained relatively constant. The initial values could *not* be restored by a standard pretreatment.

The selectivity of Rh/SiO_2 for oxidation of C_3H_6 was also time dependent. During the initial minutes of reaction, acetone was the major product, but within 1 hr, a steady state was reached with acrolein being the major product. At the conclusion of the sixth experiment with the same sample (with pretreatments between each), it was found that the selectivity to

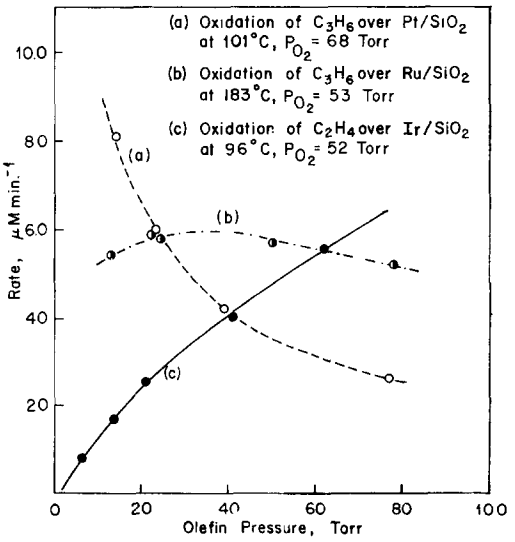

FIG. 2. Effect of olefin pressure on the rate of formation of H_2O.

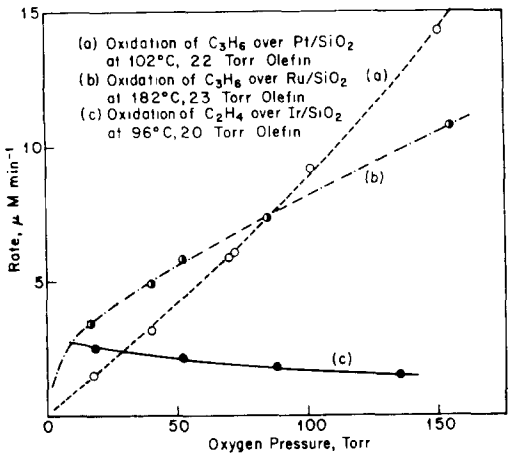

FIG. 3. Effect of oxygen pressure on the rate of formation of H_2O.

acrolein had declined from 24 to 13% under identical conditions, although the other products were still being produced at about the same rate and the activity of the sample for total oxidation to carbon dioxide and water remained unchanged. The ratio acrolein/acetone fell between 2 and 3 with both Ru and Rh, with the latter producing relatively more C_3 and less C_2 products.

The major partial oxidation product from the oxidation of C_3H_6 over Ir/SiO_2 was acetic acid and the ratio acrolein/acetone was much less than 1. Appreciable amounts of C_3 acids were also produced and mass spectral measurements indicated that this fraction consisted of about ⅔ propionic acid and ⅓ acrylic acid. With this metal, the selectivities to all products were time invariant. The Pd and Pt were relatively unselective for propylene oxidation. The former produced small amounts of acrolein, acetone, and acetic acid, while trace quantities of acetic acid and acrolein were found over the latter.

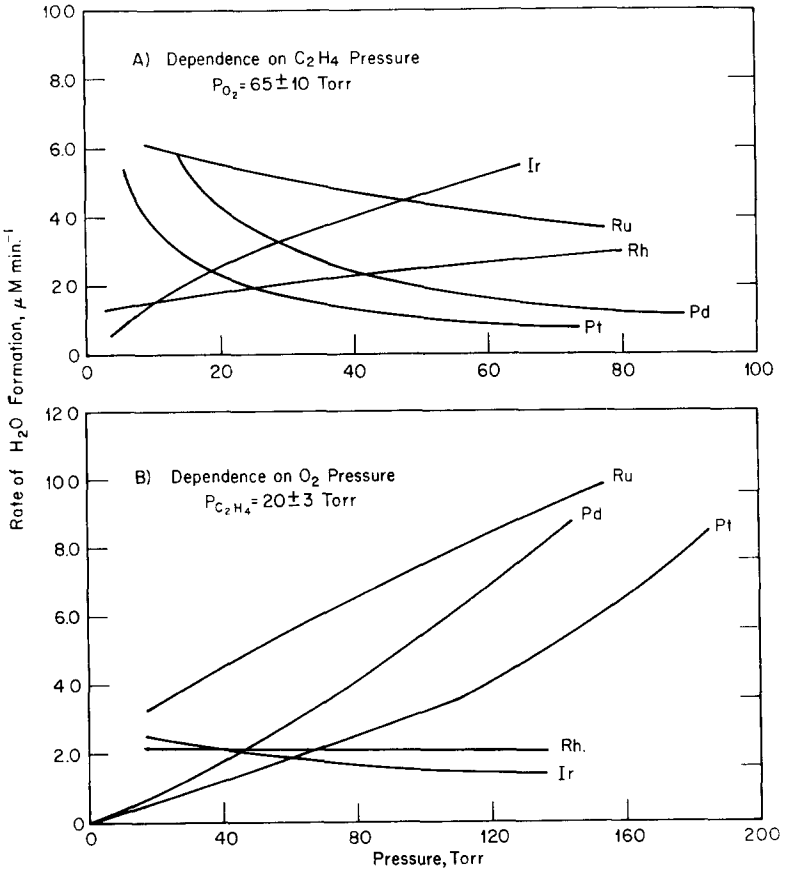

FIG. 4. Pressure dependencies for ethylene oxidation over noble metals.

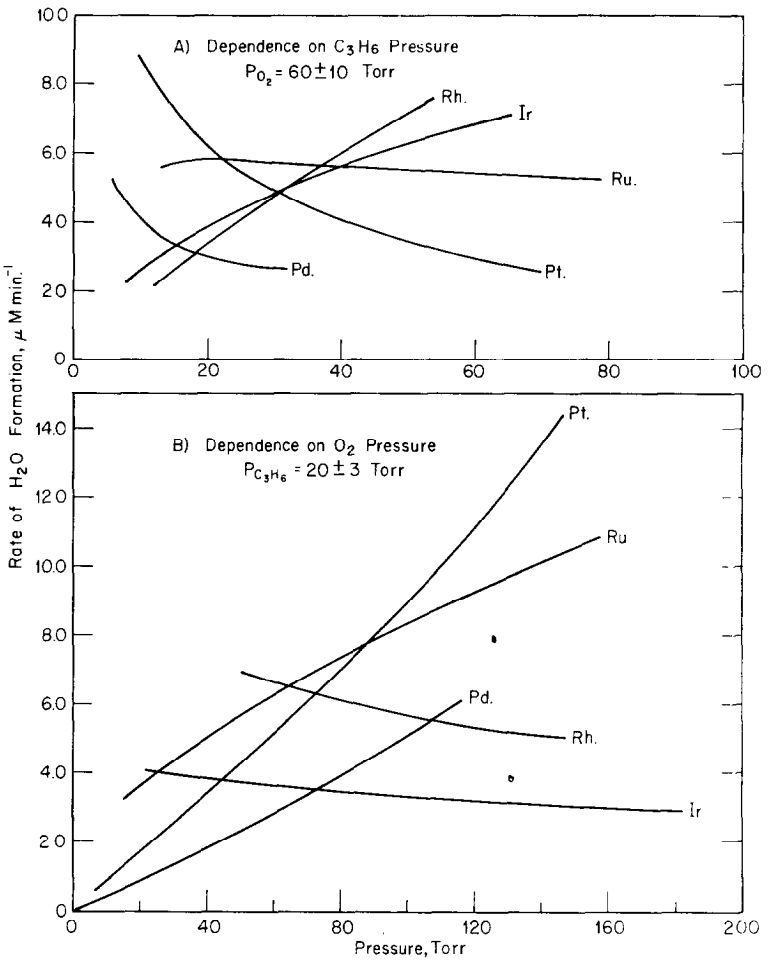

FIG. 5. Pressure dependencies for propylene oxidation over noble metals.

Three distinct types of response were characterized for the effect of changes in oxygen and olefin partial pressures on the rate of total oxidation (to CO_2 and H_2O). These are exemplified in Figs. 2 and 3. For each metal, the behavior was similar for both olefins. All of the data are given in Figs. 4 and 5, where the points have been omitted to avoid confusion. Over Pt and Pd (Type I), the rate was strongly re-

TABLE 3

KINETIC PARAMETERS FOR TOTAL OXIDATION OF ETHYLENE OVER SILICA-SUPPORTED NOBLE METALS

Metal	Metal surface area (m^2 g^{-1} of catalyst)	Pressure dependency	Apparent activation energy (kcal $mole^{-1}$)	Log A (olefin molecules sec^{-1} cm^{-2})	Temp. for standard[a] activity (°C)
Ru	3.7	II	25.8 ± 1.4	24.9 ± 0.7	162
Rh	5.3	III	25.4 ± 1.1	23.8 ± 0.5	198
Pd	0.92	I	20.4 ± 0.9	24.4 ± 0.5	87
Ir	7.3	III	16.9 ± 0.3	21.1 ± 0.2	130
Pt	1.36	I	18.5 ± 0.5	23.1 ± 0.5	91

[a] Temperature for oxidation of 10^{12} olefin molecules sec^{-1} cm^{-2} at $P_{C_2H_4} = 20$ Torr and $P_{O_2} = 65$ Torr.

TABLE 4

KINETIC PARAMETERS FOR TOTAL OXIDATION OF PROPYLENE OVER SILICA-SUPPORTED NOBLE METALS

Metal	Metal surface area ($m^2\ g^{-1}$ of catalyst)	Pressure dependency	Apparent activation energy (kcal $mole^{-1}$)	Log A (olefin molecules $sec^{-1}\ cm^{-2}$)	Temp. for standard[a] activity (°C)
Ru	3.7	II	28.7 ± 1.7	25.6 ± 0.8	188
Rh	5.3	III	26.5 ± 0.2	24.5 ± 0.1	188
Pd	0.92	I	15.7 ± 0.2	20.6 ± 0.1	124
Ir	7.3	III	17.7 ± 0.6	21.2 ± 0.3	144
Pt	1.36	I	19.8 ± 0.7	23.6 ± 0.4	98

[a] Temperature for oxidation of 10^{12} olefin molecules $sec^{-1}\ cm^{-2}$ at $P_{C_3H_6}$ = 20 Torr and P_{O_2} = 65 Torr.

pressed by olefin and was nearly first-order in oxygen pressure as was previously found for C_2H_4 oxidation over palladium sponge (*14*). The rate of the same reaction over Ru was nearly independent of olefin pressure, but still dependent on oxygen pressure (Type II). Over Ir and Rh, the rate increased with olefin pressure and was weakly

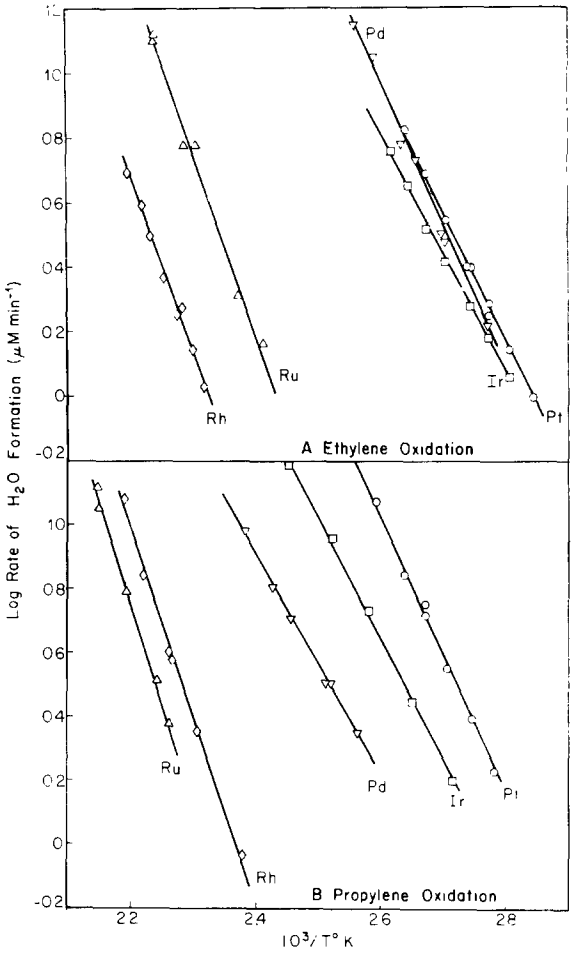

FIG. 6. Effect of temperature on rate of H_2O formation under standard conditions.

inhibited by increasing oxygen pressure (Type III). The catalysts are characterized in this way in Column 3 of Tables 3 and 4. In previous work with unsupported Pd (*14*), it was found that the rate went through a maximum at low olefin pressure near 5 Torr, i.e., the rate approached first-order in olefin pressure. Measurements could not be extended to such low pressures in the present work because holdup of oxygenated products by the support led to large errors under these conditions.

The experimentally determined surface areas of the metals in the catalysts are also given in Tables 3 and 4. Although the method of preparation was similar for each catalyst there was almost an order of magnitude difference between the most dispersed metal (Ir, 7.3 m^2 g^{-1}) and the least dispersed (Pd, 0.9 m^2 g^{-1}). The relative areas of the silica-supported catalysts of Sinfelt and Yates (*11*) showed a similar trend and indeed the absolute values for the metal areas of our catalysts were not greatly different from theirs.

Arrhenius plots for the rate of total oxidation of olefin are given in Fig. 6. Activation energies and pre-exponential factors (converted to molecules oxidized per unit of surface area per sec) derived therefrom are listed in Tables 3 and 4. In each case, the error shown refers to the standard deviation about the straight line of best fit. Over any one supported metal, the values of these quantities were similar for the oxidation of ethylene and of propylene.

The values of the kinetic parameters listed in Tables 3 and 4, and the observed pressure dependencies were used to calculate the temperatures at which each catalyst would oxidize the olefins to carbon dioxide and water at a specific rate of 10^{12}

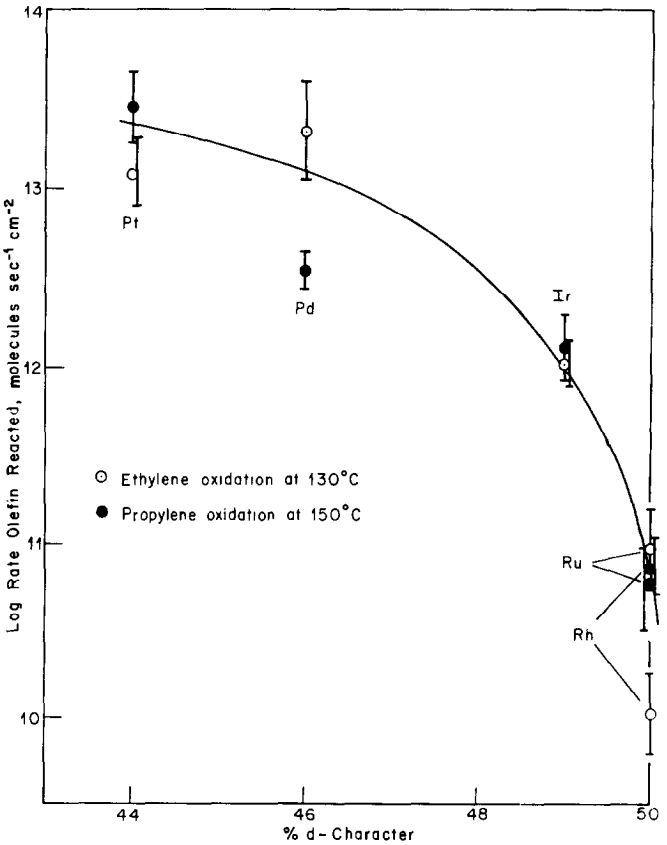

FIG. 7. Dependence of oxidation rate on percentage *d*-character of metal.

molecules cm^{-2} sec^{-1} under standard conditions (olefin pressure, 20 Torr; oxygen pressure, 65 Torr). These temperatures, which could be reproduced to ±2°C, both in duplicate experiments on the same sample (pretreated before each experiment) and in separate experiments using other samples of the same catalyst batch, are listed in the final column of Tables 3 and 4. The approximate order of activity for both reactions was Pt ⩾ Pd > Ir > Ru ⩾ Rh.

The more conventional way of comparing activities is by listing the specific rates at a given temperature. For this purpose, temperatures of 130°C for ethylene oxidation and 150°C for propylene oxidation were chosen, because these values were the approximate means of the temperatures used in the experiments. Plots of log specific oxidation rate (at these temperatures and under the standard pressure conditions) vs. the percentage *d*-character of the metals (an electronic factor) and vs. the atomic radius (a geometric factor) are shown in Figs. 7 and 8. The deviations on the points represent the 95% confidence limits of the extrapolation in rate to the temperatures chosen for comparison, together with a fixed uncertainty of 0.1 to account for possible errors (25%) in surface area measurement and correction to standard pressure conditions. Once again, the rates could be reproduced well within the limits shown. Note that the activity order was preserved.

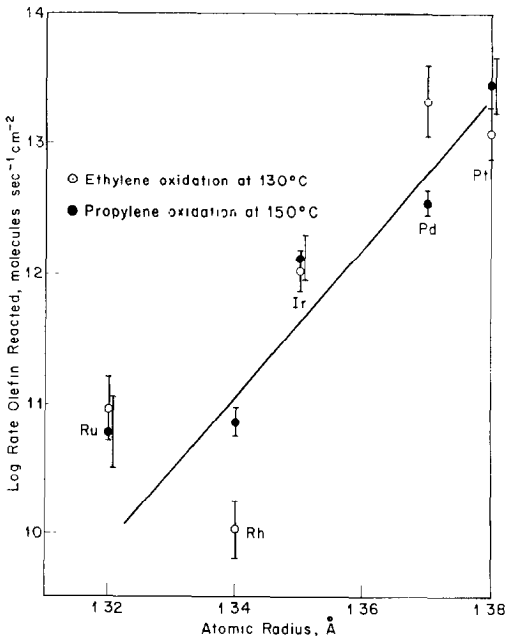

FIG. 8. Variation in rate of olefin oxidation with atomic radius of metal.

DISCUSSION

The oxidation of ethylene and propylene over Group VIII noble metals supported on α-Al_2O_3 (*15*) gave similar product distributions, respectively, to those described here. Therefore, the individual selectivities listed in Tables 1 and 2 appear to be characteristic of each particular metal. The mechanism of formation of these products will be considered later (*15*).

The kinetic data presented herein pertain to oxidation to carbon dioxide and water and the primary concern is whether or not any of the observed partial oxidation products are intermediates in the total oxidation reaction. Acetone, acetic acid, and the C_3 acids could be ruled out as intermediates because these compounds were oxidized very slowly over each one of the catalysts under conditions where olefins were oxidized rapidly. During ethylene oxidation over palladium sponge, acetaldehyde was oxidized primarily to acetic acid (*14*); and the same behavior seems likely here. Hence, these four partial oxidation products were formed by reactions independent of that leading to total oxidation. The situation with respect to acrolein was more complicated because its selectivity was conversion dependent. Furthermore, when acrolein was introduced into the reactant stream along with propylene and oxygen, a major fraction was oxidized to carbon dioxide and water. Thus, acrolein fulfills the requirements of a possible intermediate, but as yet it has not been possible to estimate the relative proportions in which carbon dioxide and water were produced from acrolein vs. a direct route, over any one catalyst. No C_2H_6 or C_3H_8 were produced during the oxidation of ethylene or propylene, even though these noble metals readily effect self-hydrogenation of olefins under non-oxidizing conditions (*16*).

The rates of the reactions were not diffusion-limited. Calculations by the methods of Satterfield and Sherwood (*17*) yielded effectiveness factors close to unity. Increasing the size of the pellets in the bed from the usual 20–30 mesh to 6–12 mesh caused no appreciable change in the specific activity under identical conditions. There were problems of heat transport, however, due to the extreme exothermicity of the reactions. Hence, the observed pressure dependencies may only approximate the true isothermal ones. A negative dependence on propylene pressure was also observed by Morooka and Ozaki (*7*) during oxidation over palladium and platinum supported on silicon carbide.

The fact that the rates of the reactions invariably showed negative dependencies on one reactant or the other suggests that the reaction occurs between two adsorbed species which must compete for surface sites. If this is so, the metals showing Type I pressure dependency would be expected to adsorb olefin more strongly than oxygen, while the reverse would be true for the metals showing Type III selectivities. Unfortunately, the necessary high coverage heat of adsorption data to test this prediction are lacking. As pointed out earlier (*14*), the negative dependence may also indicate that the rate is limited by the adsorption of the other reactant.

The type of pressure dependency did vary in a regular way with the position of the metal in the periodic table. Thus, Pd and Pt in the same column showed one behavior and Rh and Ir in the next column, another. The behavior of Ru, however, was intermediate between that of the other two, whereas its position in the periodic table would suggest an extreme situation.

The variation in the type of pressure response from metal to metal complicated attempts to relate activity to properties of the metal because the values of the specific activities are dependent upon the pressures selected for comparison. In fact, the dependence of the rate on the pressure of a given reactant may depend on the value selected for the constant pressure of the other reactant. Even the apparent activation energy depends upon the relative adsorption strengths of reactants and products in the way discussed by Bond (*18*) for Langmuir-Hinshelwood kinetics. The best that can be done without much more data is to make comparisons at low pressures and low conversions where the effects of interaction are minimal. Thus, the results listed in Tables 3 and 4 and the correlations shown in Figs. 7 and 8 must be regarded with some reservation. Further work is needed to evaluate the extent to which changes in reaction conditions can alter the results. Nevertheless, certain facts have been established. The most noticeable is that, for any one metal, the activation energies and pre-exponential factors for the oxidation of ethylene and propylene are similar. There is also a tendency for high activation energies to be accompanied by high pre-exponential factors (a compensation effect) although the correlation is not very good.

Despite the above difficulties in making activity comparisons, the order of activities is quite clear. Pd and Pt are the most active, Rh and Ru the least active, with Ir of intermediate activity. This order is the exact reverse of that observed for reactions involving hydrogen, e.g., ethane hydrogenolysis (*11*) and ethylene hydrogenation (*19*). Thus, the reason for the differing catalytic activity of the noble metals for these reactions must lie primarily in their differing abilities to activate hydrogen and oxygen, respectively, rather than in their effect on the olefin.

Morooka and Ozaki (*7*) presented evidence that the activities of metals and metal oxides for propylene oxidation are inversely related to the heats of formation of the corresponding metal–oxygen bonds (heat of formation of metal oxide per O atom). The available thermodynamic data (*20*) for the nobel metals do not offer much support for this view. There was, however, a rough inverse correlation between the heats of chemisorption (*21*) and activity. Unfortunately, data are not available for surfaces on which both gases are adsorbed; hence, the validity of such possible relationships is doubtful.

Figures 7 and 8 show that the specific activity of a metal can be correlated with

both its percentage *d*-character and its atomic radius. The correlation with both properties is not surprising since they are themselves related. Presently, correlations between catalytic and collective electron properties of solids are of dubious value. Nevertheless, the percentage *d*-character can be useful in distinguishing between correlations and relationships, as follows. This parameter refers to percentage participation of the metal atom *d*-orbitals in metal bonding (*22*). Thus, the number of *vacancies* in the *d*-orbital is, for instance, greater for Pd (46% *d*-character) than for Rh (50% *d*-character). Previously (*14*), it was shown that alloying Pd with Au, which reduced the number of vacant *d*-orbitals, resulted in a pronounced reduction in activity for ethylene oxidation. The lower activity of Rh and Ru as compared with Pd and Pt is consistent with this picture. The observed activity order is incompatible with the correlation with lattice parameter, since the lattice spacing of Pd–Au alloys is greater than that of pure Pd which is in turn greater than for Rh and Ru. Flank and Beachell (*23*), however, found a direct correlation between rate of oxidation of C_2H_4 and lattice parameter for Ag–Au alloys. Here, filling of the metal *d*-orbitals was not a factor.

The specific activities of the metals for ethylene and propylene oxidation (or the temperatures listed in the final columns of Tables 3 and 4) were also somewhat dependent on the olefin. Thus, propylene was oxidized faster than ethylene by Rh while the reverse was true for reaction over Pt and Ru. These differences were subservient to the overall pattern of metal activity, but were too large to be attributed to different pressure dependencies. Apparently, they reflect subtleties in the mechanism for each oxidation. Finally, with C_3H_6 there was a strong tendency toward an inverse relationship between activity and selectivity for formation of partial oxidation products. Whereas this could have been anticipated on intuitive grounds, its evaluation must await the development of further knowledge concerning the mechanism or mechanisms of the reactions involved.

Acknowledgment

This work was sponsored by the Gulf Research & Development Company as part of the research program of the Multiple Fellowship on Petroleum.

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