JOURNAL OF CATALYSIS 16, 204–219 (1970)

Catalytic Oxidation

I. The Oxidation of Ethylene over Pd and Pd–Au Alloys

H. R. GERBERICH, NOEL W. CANT, AND W. KEITH HALL

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

Received May 28, 1969; revised July 15, 1969

The gross kinetics for the oxidation of ethylene were determined over Pd and Pd–Au alloys in a steady-state flow reactor and in a recirculating reactor in which the products were stripped with each pass. The partial oxidation products over Pd included acetic acid, acetic anhydride, acetaldehyde, and (a trace) ethylene oxide. Initial selectivity for partial oxidation varied between 25 and 45%, depending upon reaction conditions; steady-state values fell in the range, 6–25%. Both the total rate and selectivity increased with O_2 pressure. The rates of both total and partial oxidation passed through maxima near 5 Torr with varying C_2H_4 pressure, changing from first-order at lower pressures to negative-order at higher. The apparent activation energy, based on *initial* rate data was 20 ± 2 kcal/mole for both complete and partial oxidation, but was 30 ± 2 kcal/mole for steady-state measurements. The difference may reflect effects of poisoning by products. When small amounts of acetaldehyde-^{14}C were added to the reaction, 80% of the radioactivity was recovered in the acetic acid and 10% as CO_2. Added ethylene oxide-^{14}C was recovered unreacted. The C_2H_4 reacted about 1.4 times faster than C_2D_4. Scrambling in the unreacted ethylenes during oxidation of equimolar mixtures was minimal at low ethylene pressures. No $^{16}O^{18}O$ was found when mixtures of $^{16}O_2$ and $^{18}O_2$ were used to oxidize ethylene, but the isotopic distribution in the product CO_2 was near equilibrium. The Pd–Au alloys were much less active than pure Pd and much more active than Au. The selectivity, however, went through a maximum (~50%) near 20% Pd. A similar maximum was found for fast O_2 chemisorption.

INTRODUCTION

Since Lefort's original patent (*1*), it has been well known that a substantial fraction of the products from the oxidation of ethylene over silver catalysts is ethylene oxide. This system has been extensively studied. It is unique in that Ag is the only catalyst known for ethylene oxide production and ethylene oxide is the sole partial oxidation product. It was curiosity about this situation which motivated the present work.

In 1962 Kemball and Patterson (*2*) discovered that Pd films produced small amounts of acetic anhydride and acetic acid from C_2H_4 in a reaction parallel to total oxidation (to CO_2 and H_2O). More recently, a communication from this laboratory (*3*) revealed that the selectivity for the formation of partial oxidation products could be raised from about 3% (*2*) to 30% by carrying out the reaction over Pd sponge. In the present work, results from a steady-state flow reactor are compared with those from a recirculating system. Tracer experiments were made to define some of the surface reactions occurring. The Pd–Au alloys were used as catalysts as well as pure Pd. Apart from a brief discussion in our previous communication (*3*), no information is available for ethylene oxidation over Pd–Au alloys. The variation in selectivity, rate, and kinetic behavior with catalyst composition for this system are discussed below.

Flank and Beachell (*4*) found that alloying Au with Ag lowered the activity of the latter for oxidation of C_2H_4. A correlation

was found between activity and rather small changes in lattice parameter (0.25%), which led them to suggest that a "geometric factor" was influencing the activity. The selectivity for formation of ethylene oxide increased with Au for compositions containing less than about 30 at. % Au. The activation energy fell from about 12 kcal/mole for pure Ag to 8 kcal/mole for the alloy containing 80% Au. Much larger changes (~5%) in lattice parameter occur when Pd is alloyed with Au (*5*). In addition, an "electronic factor" is introduced. Thus, comparable studies of ethylene oxidation over Pd–Au alloys afforded a way to further evaluate these factors.

The heats of formation of Pd–Au alloys are negative for all compositions (*6*), with a deep minimum near 60% Au. Since entropies of mixing are usually positive, there should be no tendency for phase separation at the surface of the type described by Sachtler and co-workers (*7*, *8*) for Cu–Ni alloys. The Pd–Au system forms a continuous series of solid solutions having minimal deviations from Vegard's law; the structure is FCC. The magnetic susceptibility falls as Au is alloyed and the system becomes diamagnetic for compositions containing less than 50% Pd (*6*). Although the alloys appear to be devoid of long-range order, the behavior of certain electrical properties has been attributed to "loose compound formation" (*9*).

Experimental Methods

Apparatus and Techniques

The reaction system used for initial rate studies consisted of a glass reactor with an internal thermocouple well and of volume about 2 ml, a pressure transducer, a trap maintained at −135°C and a magnetically operated pump. The components were connected in a cyclic manner and the reactants were circulated through the system at the pumping rate of about 75 ml/min. The transducer was catalytically inactive and its output was plotted by a recorder. The remainder of the system was made of Pyrex glass and had a volume of about 300 ml. For pretreatment, the catalyst was connected to a conventional vacuum system through a U-tube trap cooled to −78° for protection from Hg. The single-pass flow system was of conventional design. It was constructed mainly of stainless steel, but the reactor was of Pyrex glass. It has been described elsewhere (*10*).

The *standard* procedure with the recirculating system was to premix C_2H_4, O_2, and He in the proportion 1:2.3:3.3 and to admit 290 Torr of this mixture to the reaction system with the pretreated catalyst at a suitable temperature. As reaction proceeded, the condensable products were collected in the −135° trap while the unreacted C_2H_4 and O_2, together with the He and the vapor pressure of CO_2 (~1 Torr) were recirculated. Usually 10–30% of the ethylene was oxidized in each experiment. The partial pressures in the gas phase before and after reaction, and the composition of the condensed products, were determined by GLC.

In two instances, acetaldehyde-^{14}C was oxidized along with the C_2H_4–O_2 mixture. This was accomplished by diverting the recirculating gas through a second trap containing the acetaldehyde which was cooled to −78°. The collection trap was also maintained at −78° and in this way about 1 Torr of the aldehyde was recirculated until nearly all of it had been consumed. The products were separated, burned to carbon dioxide and water and the specific activities of the CO_2 (gas) samples were determined. Labeled compounds were introduced into the flow system using a Sage pump driving a gas-tight syringe.

Surface area and CO and O_2 chemisorption measurements were made with a BET system. N_2 was the adsorbate for total areas > 1 m^2 and Kr for lower total areas. Usually, the surface areas were measured after an oxidation experiment, but in several instances where they were measured both before and after, the second value was lower by about 15%.

Analytical

With both reaction systems, products were identified by comparing their chro-

matograms with those of authentic samples; where necessary, additional confirmation was obtained through mass spectral analysis and chemical tests on samples collected at the outlets from the columns. The mass spectra were taken with a 6-in. radius magnetic sector nuclide spectrometer which was also used to determine the isotopic compositions of the starting and unreacted ethylenes (at low ionization voltages) and of the acetic acid formed during experiments in which mixtures of C_2H_4 and C_2D_4 were oxidized. Specific activities of radioactive gases were determined with a Tracerlab Superscaler by methods previously described (*11*).

For the experiments with the recirculating reactor, a ⅜ in. × 3-ft column packed with 5 Å molecular sieves held at 180° was used to separate CO_2, O_2, and C_2H_4 and a ¼ in × 10-ft column containing 5% Carbowax 1500 on Fluoropak 80 at 100° for the condensable products. The corresponding columns used in the later work with the flow system were Poropak Q (¼ in × 6-ft) at 75° and Poropak R (¼ in × 5-ft) at 160°.

Catalyst and Pretreatment Method

Unless otherwise stated, the pure metal catalysts were Pd and Au sponges as received from Engelhard Industries and were stated to have purities of 99.99%. The alloys were prepared from these starting materials using two methods.

Method I was essentially that described by Kulifay (*12*) for the preparation of alloys and intermetallic compounds by reduction of the metal salts with hydrazine. Appropriate quantities of palladium and gold were dissolved separately in aqua regia and the solutions were mixed. The solution containing the reducing agent was prepared by mixing hydrazine dihydrochloride, ammonium hydroxide, and water in the proportions of 1:15:4.5 by weight, respectively; the ratio of hydrazine to the metal was 13 moles/g-atom. The hydrazine solution was heated to the boiling point, stirred vigorously while the metal salt solution was added dropwise over a 15–30-min period. A black precipitate formed immediately, but the mixture was boiled for 1 hr on completion of the reaction. The precipitate was washed repeatedly with large volumes of boiling water and dried at 125°.

Method II was reduction of the metal salts with sodium borohydride and was almost identical to that used by McKee (*13*). The metals were dissolved together in aqua regia and then reduced by rapid addition (5 sec) of a second solution containing 5% $NaBH_4$ and 9% NaOH. (It was found that if the sodium borohydride solution was added slowly the gold precipitated first.) The precipitate was washed once with dilute HCl, then repeatedly with liter quantities of boiling water until the wash solution was free of chloride (no ppt with $AgNO_3$) and had a pH of 6–7. Finally, the precipitate was dried at 125°.

Debye-Scherrer X-ray diffraction patterns of catalysts prepared by both methods and sintered at 300° showed that they were homogeneous alloys with lattice parameters in fairly good agreement with those given by Maeland and Flanagan (*5*) for Pd–Au alloys prepared by melting. However, spectrographic analyses showed that the impurity content was dependent on the method of preparation. Alloys prepared by Method II contained up to 2000 ppm of B and 10–15 ppm of Na while the starting materials and the alloys prepared by Method I contained only 3–10 ppm of Na. The level of other impurity elements were comparable in all samples and amounted to a total of 130–250 ppm for Cr, Cu, Fe, Ag, and Ni.

Prior to each experiment, the catalyst sample was reduced in flowing hydrogen at either 300° (alloys) or 500° (pure metal sponges) for 2–6 hr and then freed from hydrogen by either evacuation or purging with helium for 15–20 hr at the same temperature.

Materials

The chemicals used in alloy preparation were sodium borohydride (98%) and hydrazine dihydrochloride (Certified Reagent 100.5% assay), both from Fisher Scientific Co.; NH_4OH, HCl, and HNO_3 were Baker

and Adamson (Research Grade) materials. All water was distilled and then demineralized.

The gases employed with the recycle reactor were purified as follows. Ethylene (Phillips Research Grade 99.97% pure) was passed through a trap at —78°, and given a repeated freeze–pump–thaw treatment at —196°. Carbon monoxide (Matheson C.P. 99.5%) was passed through a trap at —183°. Oxygen (Linde USP, 99.5%) and helium (Airco C.P. 99.95%) were passed over activated charcoal at —78 and —196°, respectively. Hydrogen (Airco Electrolytic Grade 99.95%) was passed through a Deoxo unit, over Pt asbestos at 350° and finally over charcoal at —196°. In flow experiments, the gases were purified as described elsewhere (*10*).

The CH_3CHO-1,2-^{14}C (Baird Atomic, Inc.) was diluted with Eastman White Label acetaldehyde. Radioactive ethylene oxide (^{14}C) was also obtained from Baird Atomic and was diluted with Matheson C.P. grade ethylene oxide prior to use. Deuterated ethylene ($C_2D_4 > 99\%$ D) was obtained from Volk, Inc.; $^{18}O_2$ (97%) was purchased from Yeda Research and Development Co. These reagents were used as supplied.

Treatment of Data

When using the steady-state reactor, condensable products were collected for fixed time intervals in a sampling loop cooled with either dry ice or liquid nitrogen (*10*). The rates of formation of each product were calculated directly (μM min^{-1}) from the chromatogram of total collected product. These data could be readily converted into an oxidation rate (C_2H_4 molecules sec^{-1} cm^{-2}) using the surface area data and the known stoichiometry of the reactions. For reaction in the recirculating system, the initial and final partial pressures of ethylene and oxygen were known from the GLC analyses. By assuming that the changes in these quantities were linear with overall pressure decrease, it was possible to convert the experimental curve of overall pressure vs. time to a plot of ethylene pressure vs. time. The specific rate at any time could then be calculated from the slope of this plot, knowing the volume of the system and the surface area of the catalyst.

With both systems, the selectivity was calculated from the analysis of products accumulated in the trap and was defined as 100 times the number of moles of ethylene converted to acetaldehyde, acetic acid, and acetic anhydride divided by the total number of moles of ethylene oxidized to all products.

Results

Initial Rate Studies over Pure Palladium

Partial oxidation products positively identified during ethylene oxidation over palladium included acetic acid, acetic anhydride, acetaldehyde, and ethylene oxide (trace). The initial selectivity to partial oxidation products was in the range 25–40%. Of these products, acetaldehyde comprised 1–10%; acetic acid was always the major product although some of this may have been formed by hydrolysis of acetic anhydride during collection.

Several representative ethylene pressure vs. time curves for oxidation over pure palladium (2.05 g, 0.2 m^2 g^{-1} pretreated at 500°), using the standard mixture in the recirculating system, are shown (open symbols) in Fig. 1. The plots were usually

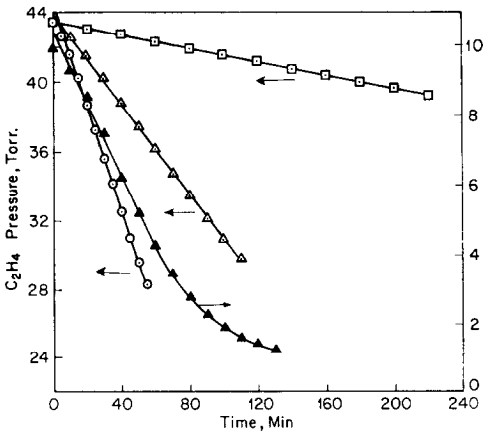


FIG. 1. Rates of oxidation of ethylene over pure palladium; in a recirculating reactor at (°): 71, ⊡; 91, △; 92, ▲; and 103, ⊙.

nearly linear, so an accurate value for the *initial* rate could be calculated from their slopes.

The apparent activation energy, calculated from an extended series of curves of this type, was 20 ± 1 kcal mole^{-1}. Since the initial selectivity changed only slightly with temperature (38% at 78°, 33% at 109°), the difference in activation energy for partial and total oxidation was small (<1 kcal mole^{-1}). The overall pre-exponential factor was 4×10^{24} C_2H_4 molecules sec^{-1} cm^{-2}.

It could not be concluded from these curves that the reaction was zero-order in C_2H_4 because the pressures of both reactants were falling simultaneously by similar fractions and a positive dependence on the pressure of one reactant could be canceled by a negative dependence on the other. In experiments in which the initial ethylene pressure was lowered to 10 Torr from 44 while the oxygen pressure was kept constant at 100 Torr, the curves were fairly linear until the C_2H_4 pressure fell below 5 Torr (e.g., see filled triangles of Fig. 1). Below this limit, the slope decreased continuously, indicating a change in the reaction order in this region.

Experiments were made to determine the effect of reactant pressure on the initial rate and selectivity. At 90° with a constant O_2 pressure of 100 ± 3 Torr, the initial rate appeared to be independent of C_2H_4 pressure in the range 10–47 Torr; the average values at 44 and 10 Torr were $4.4 \pm 0.6 \times 10^{12}$ and $4.8 \pm 0.2 \times 10^{12}$ molecules sec^{-1} cm^{-2}, respectively. The observed selectivities were also constant at $35 \pm 4\%$. By contrast, with a constant C_2H_4 pressure (44 ± 3 mm) both the rate and selectivity varied with O_2 pressure as shown in Fig. 2. The selectivity increased from about 25% for an oxygen pressure of 25 Torr to about 43% when the oxygen pressure was 250 Torr. The rate of total oxidation was about first-order in O_2 pressure at low pressures, but tended towards half-order at high pressures.

It would be expected from these apparent kinetics that, under standard conditions, the rate would fall with time in

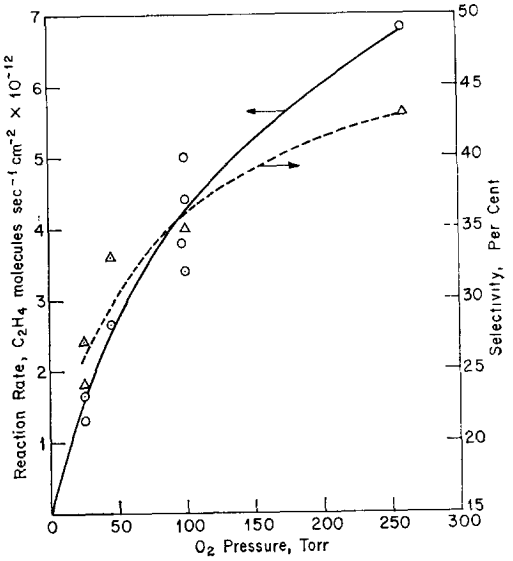


FIG. 2. Effect of oxygen pressure on initial rate of oxidation and on selectivity over pure palladium at 90 ± 1°C; ethylene pressure was constant at 44 ± 3 Torr.

direct proportion to the oxygen pressure rather than follow the observed linear paths (Fig. 1). In experiments with a higher surface area palladium sample (prepared by Method I, 1.75 g, 1 m^2 g^{-1} pretreated at 300°), the slope of the ethylene pressure vs. time curve did decrease as the reaction proceeded, although the initial specific rate, under standard conditions at a given temperature, was within experimental error (±20%) of that measured with the lower area catalysts. It was these kinetic inconsistencies and the presence of poisoning which led us to make some additional experiments with a steady-state system.

Material balance calculations showed that 2–6% of the reactants were being retained by the catalyst in each experiment. Qualitatively, the amount adsorbed was smallest at the highest temperature and largest at the lowest temperatures and was directly related to the surface area of the catalyst sample. This accumulation of residue probably accounted for some of the decrease in activity with time.

Steady-state experiments over pure palladium. With the single-pass system, the method corresponding to the *standard pro-*

TABLE 1
VARIATION IN RATE OF ETHYLENE OXIDATION OVER Pd SPONGE WITH TIME[a]

Elapsed time (hr)	Reaction temp. (°C)	Rate of C_2H_4 consumption (μM min^{-1})	Rate of H_2O formation (μM min^{-1})	Selectivity,% to CH_3COOH + $(CH_3CO)_2O$	Selectivity,% to CH_3CHO[b]
0 5	81.8	7.7	12 4	27.	
1.0	81.4	6.6	10.7	27.	1.2
1.5	80.4	4.8	7.73	26.	
2.2	79.6	2.7	4.43	25.	1.1
3.1	79.2	2.0	3.29	20.	
3.6	79.2	1.7	2.87	19.	1.3
4.1	79.1	1.4	2.51	17.	
4.7	79.1	1.3	2.18	18.	2.2
5.2	79.1	1.2	2.04	17.	
5.8	79.1	1.1	1.84	18.	2.4
6.3	79.0	1.1	1.86	17.	
23	78.6	0.6	1.01	18.	

[a] Experiments were made with the steady state flow system; $P_{C_2H_4} = 40 \pm 2$ Torr, $P_{O_2} = 98 \pm 3$ Torr and a total flow rate of 45 ml min^{-1}. The catalyst was prepared by Method I and weighed 4.28 g reduced. Its surface area was 1.0 m^2 g^{-1}.

[b] Some ethylene oxide is included.

cedure in the recirculating system was to flow a mixture of ethylene, oxygen, and helium at partial pressures of 40, 100, and ~600 Torr, respectively, over the catalyst at a constant total flow rate of 45 ml (NTP) min^{-1}. In some instances, 90 ml (NTP) min^{-1} were used and these experiments are specifically designated. Using this method, it was found that the activity of a Pd catalyst changed markedly with time in the way shown in Table 1. Over the first 24 hr, the rate declined by an order of magnitude and the selectivity fell to about half its initial value. The initial values could be substantially restored, however, by a standard pretreatment so that the observed decline was not due to permanent loss of surface area. Following the "lining-out" period, the catalytic activity remained constant for many days.

The effect of changes in temperature on the lined-out activity are given in Fig. 3, where the points are numbered in the order the data were taken. Between each determination an hour elapsed, except for point 10 which was obtained 16 hr after point 9. When the points around $10^3/T = 2.59$ were examined, the rates were found to be somewhat dependent upon whether the previous temperature was higher or lower than this value. If, however, sufficient time was allowed for the stabilization, the rate was quite reproducible (compare points 1 and 10, 24 hr apart). The apparent activation energy was the same (30 ± 2 kcal/mole) for both partial and total oxidation

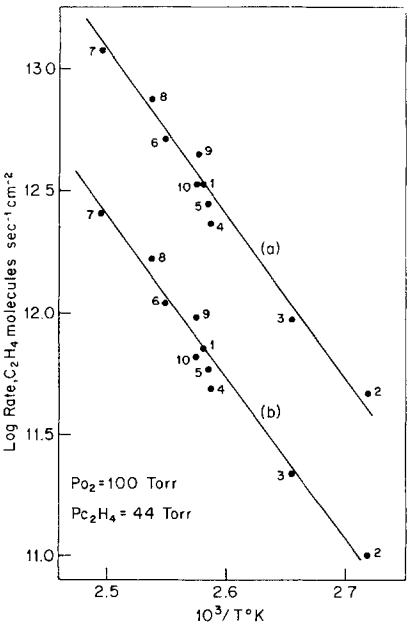


FIG. 3. Effect of temperature on rate of (a) total oxidation, (b) partial oxidation.

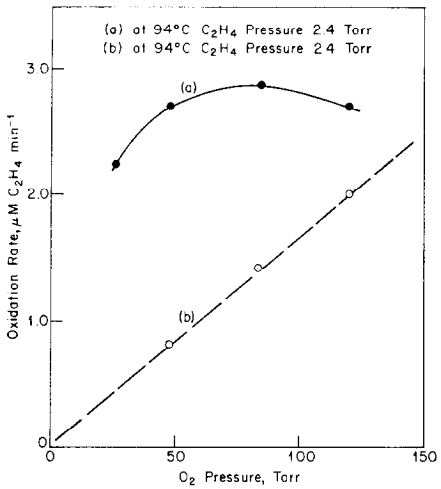


FIG. 4. Effect of oxygen pressure on oxidation rate to water over palladium sponge.

(Fig. 3). This meant that the selectivity was constant (at 14–17% under standard conditions), irrespective of the temperature.

The reaction was also rather sluggish in responding to changes in reactant pressure. Our most reliable results were obtained using a 4.34-g sample of the palladium sponge (surface area 0.2 m^2 g^{-1}) and a total flow rate of 90 ml min^{-1}; these data are shown in Figs. 4 and 5. With a constant ethylene pressure of 24 Torr (Curve b), the rate was first-order in oxygen. However, when an ethylene pressure of 2.4 Torr was employed (Curve a), the dependence was closer to zero-order, as was observed by Kemball and Patterson (*2*) in their experiments with a similar ethylene pressure. These authors stated that the dependence of the rate on ethylene pressure (with an oxygen pressure of 23 Torr) was first-order below 2.3 Torr and zero-order above this limit. However, their experimental data, which is also plotted in Fig. 5, agreed quite well with ours. There seems little doubt then, that the rate goes through a maximum with ethylene pressure in the range 1–10 Torr. Under *standard* conditions, the pressure dependencies were, therefore, first-order in oxygen, but inverse in ethylene and the near linear plots of Fig. 1 are quite understandable on this basis.

The effect of reactant pressures on the

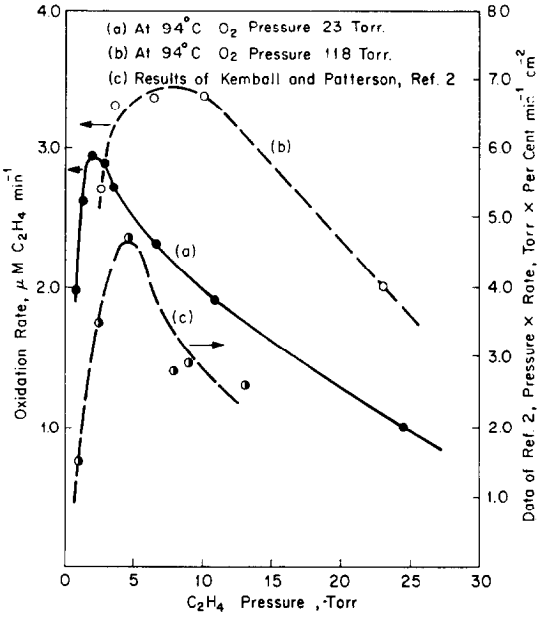


FIG. 5. Effect of ethylene pressure on rate of total oxidation over palladium sponge.

rate of partial oxidation is demonstrated in Figs. 6 and 7, where the numbers refer to the percentage selectivity. The kinetic behavior was quite similar to that observed for complete oxidation, although the rate

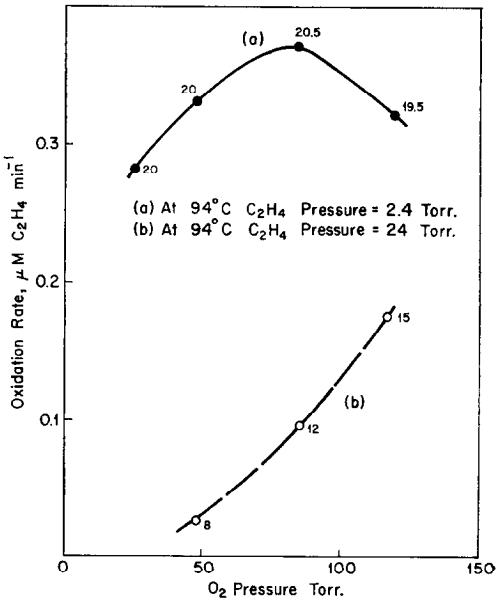


FIG. 6. Effect of oxygen pressure on rate of oxidation to acetic acid over palladium sponge.

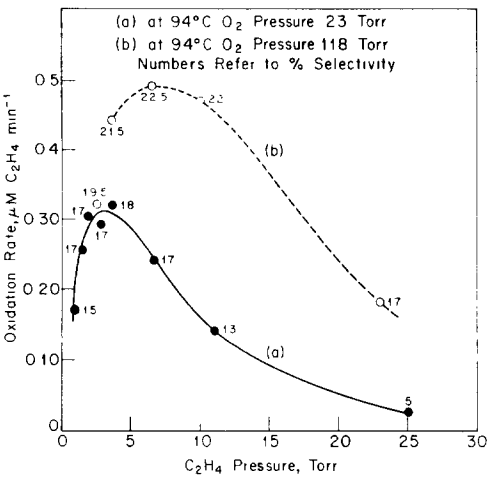


FIG. 7. Effect of ethylene pressure on rate of oxidation to acetic acid over palladium sponge.

of partial oxidation fell off more sharply for a given increase in ethylene pressure and also increased more rapidly with oxygen pressure. Thus, high selectivities under "lined-out" conditions are favored by ethylene pressures in the range 2–10 Torr and the highest possible oxygen pressure. It is noteworthy that these same conditions also maximize the overall oxidation rate.

Product Poisoning

The effects of reaction products were investigated. A syringe driven at a constant rate was used to introduce the compound immediately upstream from the catalyst in the flow reactor. CO_2 was without effect on the rate or selectivity. When H_2O was introduced at a rate approximately equal to its rate of formation by oxidation, total oxidation was suppressed by about 10%, but partial oxidation was unaffected; hence, a small increase in selectivity resulted. Acetic acid and acetic anhydride caused pronounced reduction in rate, and for a given pressure the former was approximately three times as strong a poison as the latter. Acetic acid added at about the same rate as the overall rate of partial oxidation of ethylene caused a 20% decline in water formation. Since the partial pressure of the added acetic acid was only about 10% that of the added H_2O and since its effect on the rate was larger, acetic acid was the stronger poison, perhaps by an order of magnitude. In every case, once the source of added poison was removed, the original catalyst activity was restored within an hour. These results indicate that under steady-state conditions, product inhibition was present to some extent. However, because of the low conversions involved, the pressure dependencies revealed by Figs. 4–7 were not greatly affected by these factors. Consequently, they probably represent the true kinetics of reaction quite closely.

Tracer Studies During Ethylene Oxidation

The formation of small amounts of acetaldehyde during ethylene oxidation over palladium was positively established in our experiments. The results of two experiments in which mixtures of ethylene and acetaldehyde-^{14}C were cooxidized in the recirculating system are summarized in Table 2. In these experiments, the gas was recirculated until several times more C_2H_4 was consumed than acetaldehyde added (see "Experimental Methods" section). Over pure Pd, less than 10% of the total radioactivity ended up in the CO_2 while nearly 80% was in the acetic acid. This provided good evidence for the validity of the suggestion of Kemball and Patterson (*2*) that acetaldehyde is an intermediate for acetic acid formation and that partial and complete oxidation are primarily parallel rather than consecutive reactions. By contrast formic acid (and probably formaldehyde as well) was rapidly oxidized to $CO_2 + H_2O$. Results with the alloy catalyst were generally consistent with the data for pure Pd (*vide infra*).

An experiment was also carried out in which a mixture of ethylene oxide-^{14}C, C_2H_4, O_2, and He with respective pressures of 1.5, 12, 100, and 625 Torr, was passed over Pd (prepared by Method I, 4.28 g, surface area 1.0 m^2 g^{-1}) at 45 ml min^{-1} and at a temperature where about 30% of the ethylene was oxidized to the usual products. Substantially, all of the ethylene oxide was recovered, unreacted and unisomerized, and the radioactivity of both the acetic acid and carbon dioxide was neg-

TABLE 2
OXIDATION OF ETHYLENE WITH ADDED ACETALDEHYDE-^{14}C

	Product	Amount formed (μM)	Sp act[c]	Location[d] of ^{14}C (%)
Over 100% Pd[a]	CO_2	201	37	6.4
	CH_3CHO } CH_3COOH }	125	719	78
Over 20% Pd[b]	CO_2	139	138	18
	CH_3CHO	12	131	1.2
	CH_3COOH	126	630	76

[a] At 72°C, with 73 μM of added CH_3CHO-1,2-^{14}C of specific activity 1598 cpm Torr^{-1} over 1.75 g of catalyst (surface area, 1 m^2 g^{-1}).

[b] At 102°C, with 68 μM of added CH_3CHO-1,2-^{14}C of specific activity 1555 cpm Torr^{-1}, over 3.65 g of catalyst (surface area, 1.0 m^2 g^{-1}).

[c] In cpm Torr^{-1}.

[d] Some of the ^{14}C was lost through adsorption on the catalyst and in handling. The values shown were calculated from [100 (sp act)(μmoles formed)]/[(1598)(μmoles of acetaldehyde used)].

ligible. This showed that ethylene oxide cannot be an intermediate for either complete or partial oxidation, although it conceivably could be formed from the same surface species as some of the other products.

On several occasions, a 1:1 mixture of C_2H_4 and C_2D_4 was oxidized to see if a kinetic isotope effect was operative in either oxidation. The isotopic compositions of unreacted ethylene and product acetic acid for two experiments are shown in Table 3. Fully deuterated acetic acid was barely detectable because the acid OD group was rapidly exchanged by sources of hydrogen on the chromatographic column used for separation. Thus, this product became d_3. When high ethylene pressures were employed, exchange among the olefin molecules was faster than the oxidation rate and meaningful kinetic isotope effects could not be measured. However, this mixing was negligible at low ethylene pressures (below 3 Torr) and k_H/k_D ratios could be calculated from substitution experiments with C_2D_4 alone and competitive experiments using C_2H_4/C_2D_4 mixtures.

The value expected for the k_H/k_D ratio (*14*) at 110° for the breaking of carbon–hydrogen as compared with a carbon–deuterium bond is in the region 3 to 4. Thus, the values observed (1.4 ± 0.1 for

TABLE 3
OXIDATION OF C_2H_4/C_2D_4 MIXTURES OVER PALLADIUM SPONGE

Expt. no.	Products analyzed	Experimental Conditions: Ethylene pressure (Torr)	Ethylene conversion (%)	Isotopic composition (%) d_0	d_1	d_2	d_3	d_4	Fraction exchanged molecules (%)	Exchange/ conversion
1[a]	Unreacted ethylenes	22	10	38.2	8.8	3.6	9.1	40.8	20	2.0
2[b]	Unreacted ethylenes	3	35	47.7	1.6	0.5	2.2	48.0	3.3	0.1
	Product acetic acid[c]			46.6	7.3	9.4	36.7		17	0.5

[a] At 90°, O_2 pressure of 65 Torr over 4.28 g of catalyst of surface area 1.0 m^2 g^{-1}.

[b] At 120°, O_2 pressure of 135 Torr over 4.34 g of catalyst of surface area 0.2 m^2 g^{-1}.

[c] Values for methyl group only; corrected for starting impurities and deuterium in carboxyl group.

total oxidation, 1.3 ± 0.1 for partial oxidation) indicate only a secondary effect and suggest that carbon–hydrogen bond cleavage is not the slow step in ethylene oxidation. Moreover, the amount of acetic acid-d_1 was much too low to be consistent with an hypothesis of one intermolecular hydrogen transfer per tranformation of C_2H_4 to CH_3CHO or CH_3COOH.

Experiments in which a 3:1 mixture of $^{16}O_2$ and $^{18}O_2$ (97%) was used to oxidize ethylene over pure palladium showed that the *unreacted* oxygens contained no $^{16}O^{18}O$. In fact, even in the absence of ethylene, the exchange reaction was not observable over freshly pretreated (reduced) Pd at temperatures below 250°. Thus, one must conclude either that ethylene oxidation over Pd does not require dissociated oxygen or that recombination and desorption of oxygen atoms is very slow. The isotopic distributions in the CO_2 and the acetic acid were, however, very close to equilibrium (e.g., 73.0% $C^{16}O_2$, 23.3% $C^{16}O^{18}O$, 3.7% $C^{18}O_2$). Separate experiments in which C_2H_4, O_2^{16} and CO_2^{18} mixtures were flowed over Pd under standard conditions established that no oxygen transfer took place between the CO_2^{18} and the CO_2^{16} being formed by C_2H_4 oxidation.

Oxidation over Palladium–Gold Alloys

Ethylene oxidation was studied over seven Pd–Au alloys at 100°, using the standard procedure in the circulating system. The observed variation in initial rate with composition is shown in Fig. 8. Within the estimated error, the initial rate was fairly independent of composition in the range 16–75% Pd, although this value was two orders of magnitude less than that for pure Pd and was greater by a similar factor than that for pure gold (based on extrapolation of the rates determined at a higher temperature).

The initial selectivity at 100° over alloys prepared by Method I varied with alloy composition in the way shown in Fig. 9. It was low for alloys having palladium contents in the range 40–80% or less than 15%, but went through a steep maximum near 20%. Initial rate and selectivity determinations under standard conditions at other temperatures revealed similar patterns, but the results were too imprecise to yield a complete picture of the effect of composition on the apparent activation energy.

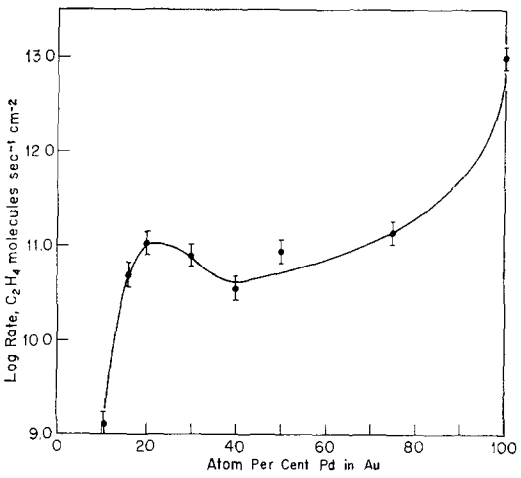


FIG. 8. Oxidation rate as a function of alloy composition under standard conditions at 100°C.

Significantly, only over the 20% alloy was acetaldehyde formed in more than trace amounts. At 70°, the overall selectivity was 70%, comprising acetaldehyde and acetic acid (plus acetic anhydride) in nearly equal amounts; at 100°, the selectivity was 50% of which acetaldehyde amounted to about one fifth, while at 130° the selectivity decreased to 30% and only

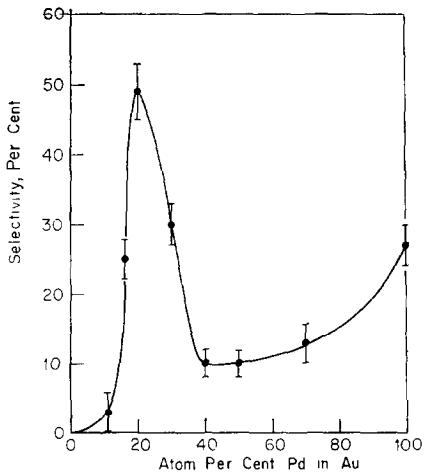


FIG. 9. Selectivity at 100°C as a function of alloy composition.

a trace of acetaldehyde was detected. From these observations, it might be supposed that at the higher temperatures, acetaldehyde was being oxidized to CO_2 rather than acetic acid. However, tracer experiment over the alloy catalyst (Table 2) showed that most of the radioactivity appeared in the acetic acid rather than the CO_2. Also, the ratio of the specific activity of the acetaldehyde to that of the acetic acid was 0.17, showing that most of the radioactive acetaldehyde had reacted and had been replaced with molecules formed by ethylene oxidation. Thus partial and complete oxidation are parallel reactions over the alloy catalyst also and the variation in selectivity with temperature must be the result of a difference in activation energy for the two reactions. This difference was estimated to be 6 kcal mole^{-1} compared with less than 1 kcal mole^{-1} for the same two reactions over Pd.

These rate and selectivity data for ethylene oxidation over the Pd–Au alloys were confirmed by experiments carried out with the single-pass flow system. Such experiments also served to show that poisoning of the alloy catalysts proceeded in a similar way to that described for pure Pd, although the rate of poisoning was temperature dependent and by no means the same for all alloys.

Eventually a steady state could be reached for each alloy, but the selectivity in this state was invariably low (less than 5% regardless of composition). Activation energies and pre-exponential factors calculated from these data are given in Table 4. Both of these quantities increased with Pd content and there was an approximately linear relationship between them (compensation effect). No attempt was made to determine the steady-state reaction kinetics for all alloys, but limited measurements with the 20% alloy gave the results shown in Fig. 10. As with Pd, the reaction was first-order in oxygen and went through a maximum with ethylene. However, under equivalent conditions, the alloy required a much higher ethylene pressure to achieve the maximum rate.

TABLE 4
ACTIVATION ENERGIES AND PRE-EXPONENTIAL FACTORS FOR STEADY STATE OXIDATION OF ETHYLENE OVER Pd–Au ALLOYS

Palladium (%)	Surface area (m^2 g^{-1})	Activation energy (kcal mole^{-1})	$\log_{10} A$ (molecules sec^{-1} cm^{-2})
100	0.2	30 ± 1.7[a]	29.9 ± 1.0[a]
50	3.5	25.6 ± 2.6	25.1 ± 1.4
40	3.1	20.2 ± 1.0	21.7 ± 0.5
20	1.0	21.2 ± 1.8	21.6 ± 0.8

[a] These errors refer to calculated standard deviations.

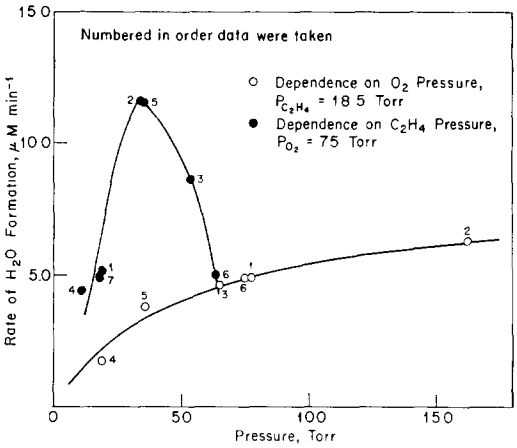


FIG. 10. Pressure dependencies in ethylene oxidation over 20% Pd–Au alloy at 185°C.

Carbon Monoxide Chemisorption

The chemisorption of carbon monoxide at 100 Torr was measured at 0° after a 30-min contact with the surface and at 100° after an additional 30 min. The adsorption at each temperature was fast and complete after a few minutes. The chemisorption data taken at 100° are plotted in Fig. 11 as a function of alloy composition. All of the data fell close to a straight line passing through the origin. Similar behavior was observed at 0°, although the slope of the line was a little less. When adsorption measurements at 100° were continued beyond 30 min, a very slow uptake occurred over a period of many hours. This additional adsorption varied with alloy composition, but never exceeded 20% of that taken up in the initial 30 min. The

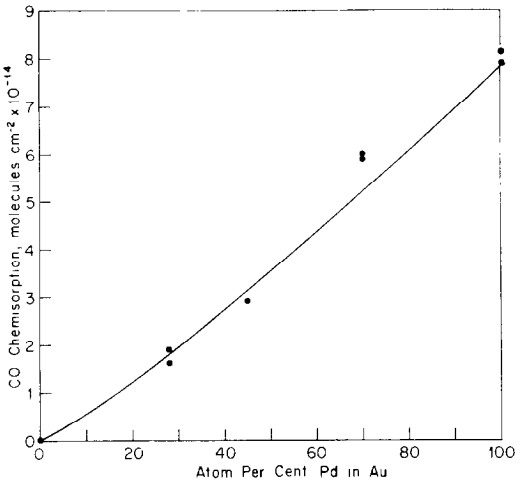


FIG. 11. Chemisorption of CO at 100°C and 100 Torr on Pd–Au alloys as a function of alloy composition.

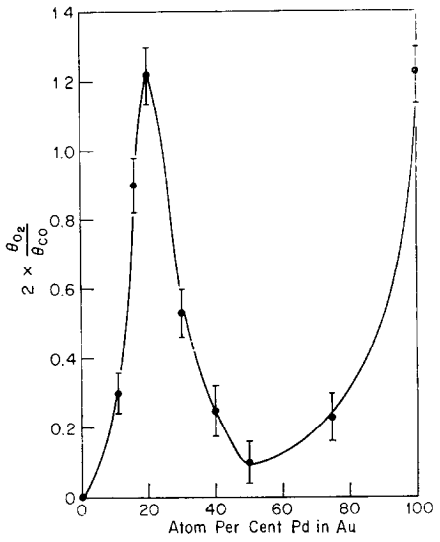


FIG. 12. Ratio of oxygen chemisorption to carbon monoxide chemisorption at 100°C as a function of alloy composition.

data suggest that nearly a complete monolayer is adsorbed on Pd and that adsorption on Au is nil.

Chemisorption of Oxygen

An attempt was made to assess the rates of oxygen chemisorption on these catalysts. A constant volume system was used and the chemisorption was measured as a function of time. The small magnitude of this parameter with some catalysts dictated the use of low pressures ($\leqslant$10 Torr) to achieve reasonable accuracy. Two types of chemisorption were distinguished: a very rapid initial chemisorption (complete in about 10 min) and a slow process following Elovich kinetics. The rate of the fast process decreased rapidly with coverage, the adsorption during the first minute being about half the total adsorption during the first ten. It was ascertained that the rate of oxidation (based on O_2 consumption) fell between the rate of chemisorption during the first minute and the average rate over the next nine. This comparison was possible because the chemisorption rates were not very pressure dependent.

The slow chemisorption may have involved bulk oxidation, because after several days the volume adsorbed exceeded one oxygen atom per surface Pd. The presence of C_2H_4 virtually eliminated this process.

The total chemisorption during the first 10 min increased slowly with an increase in temperature, but at a given temperature it varied considerably with alloy composition. When these data (for 100°) were normalized to the corresponding CO chemisorptions (to give O atoms adsorbed per surface Pd), a curve strikingly similar to Fig. 9 was evolved; this is shown in Fig. 12. In accordance with the observation that the selectivity increased with O_2 pressure, the selectivity was maximized by saturation of the surface Pd atoms with chemisorbed oxygen.

DISCUSSION

The kinetics of the Pd-catalyzed oxidation of C_2H_4 to CO_2 and H_2O, reported herein, are in good agreement with the findings of Kemball and Patterson (*2*) provided comparison is made in similar pressure ranges. At first sight, the pressure dependencies under our standard conditions (first-order in oxygen and about negative first-order in olefin) may seem rather strange, but a similar behavior has been observed many times during CO oxidation

over Pd [see discussion of Baddour *et al.* (*15*)].

The gross kinetics were qualitatively similar for partial oxidation and total oxidation and over the alloy and pure Pd catalysts. The same activation energy was found for both total and partial oxidation. It may be concluded, therefore, that the controlling factors are the same in all these cases, and perhaps for CO oxidation as well.

As pointed out by Kemball and Patterson (*2*), the heat of adsorption of oxygen (*16*) at low coverages is higher than that of ethylene (*17*). What cannot be assessed are the relative heats and coverages under reaction conditions. On the basis of the available data, it seems likely that at the low pressures used by Kemball and Patterson, the surface is predominantly covered with oxygen, with ethylene adsorbed on top or in between the chemisorbed oxygen atoms. The kinetics then approach zero-order in oxygen and first-order in C_2H_4 as reported (*2*). At higher C_2H_4 pressures, the kinetics approach first-order in O_2 and negative first-order in C_2H_4 pressure. These data suggest that the surface is heavily covered with C_2H_4 (or residues formed therefrom), under these reaction conditions, making adsorption of oxygen rate determining. This is supported by the fact that $^{16}O_2$ did not exchange with $^{18}O_2$ under reaction conditions, although the CO_2 formed was close to equilibrium. It is also supported by the observation that some isotopic scrambling occurred when mixtures of C_2H_4 and C_2D_4 were cooxidized, showing that these molecules do undergo desorption. No $^{16}O^{18}O$ was formed over the clean surface in the absence of C_2H_4 at the temperature of the oxidation reaction, but this is irrelevant. Oxygen is dissociated during reaction, but it does not desorb under our experimental conditions. Thus, there is a strong analogy between oxidation and hydrogenation of C_2H_4 over metal surfaces.

The data can be discussed in a general way on the basis of the Langmuir-Hinshelwood model. For the case of reaction between two adsorbed species, the negative dependence on C_2H_4 pressure is evolved, if it is assumed that C_2H_4 is more strongly adsorbed than oxygen. The first-order dependence on oxygen pressure requires, however, that molecular oxygen compete for surface sites with C_2H_4. It was not found possible to fit the observed kinetics over the entire pressure ranges with a unique set of Langmuir-Hinshelwood parameters.

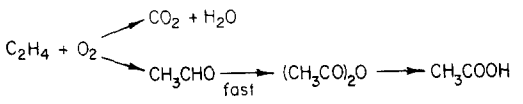
The high values of the pre-exponential factors recorded in the present and related work (*2, 10, 18*) for this reaction deserve comment. Most values of log A fell between 20 and 25 with several values somewhat higher. The collision frequency of O_2 with the surface under the experimental conditions is $\sim 10^{23}$ sec^{-1}. This, together with the fact that the absolute rate of reaction was of the same order of magnitude as the observed rate of oxygen chemisorption on the partially oxidized surface, supports the idea that oxygen chemisorption is the rate limiting step. This assumption would also explain the absence of a kinetic isotope effect in comparison of the oxidation rates of C_2H_4 and C_2D_4, although other explanations could be advanced. The equation

$$\text{rate} = kP_{O_2}(1 - \theta_E)$$

leads to the desired pressure dependencies when $KP \gg 1$. Here, θ_E is the fraction of the surface covered with C_2H_4 and KP is a term of the Langmuir equation.

In their work, Kemball and Patterson (*2*) found an apparent activation energy of 14 kcal mole^{-1}, compared with 20 kcal mole^{-1} (based on initial rates) and 30 kcal mole^{-1} (steady-state conditions) reported herein. These discrepancies can be expected since the mechanism is not the same at high and low ethylene pressures and since reversible poisons will play a role under steady-state conditions. A more quantitative discussion would require the postulation of particular mechanisms and this is unwarranted on the basis of the available information.

One of the chief conclusions of Kemball and Patterson (*2*) was that ethylene oxidation proceeded by two parallel paths as follows:



Our tracer experiment with ^{14}C-labeled acetaldehyde showed that most of the CO_2 and H_2O was indeed formed directly from C_2H_4, i.e., that acetic acid and acetic anhydride were much more refractory than C_2H_4. One of the advantages of the flow reactor was that it enabled us to positively identify small amounts of acetaldehyde and even smaller quantities of ethylene oxide.

One salient difference between our results and those of Kemball and Patterson (*2*) is in the value for the selectivity. They reported that less than 3% of the ethylene was oxidized to useful products, whereas we found values 5–15 times greater under comparable conditions. They used a static system which allowed an accumulation of acetic acid on the metal surface. Preferential poisoning of partial oxidation sites could have produced their lower selectivities. In our experiments, the selectivity increased with oxygen pressure; it could also be increased by alloying more than 60% Au with Pd. These results suggest that total oxidation is related in some way with the ability to dehydrogenate the olefin. Hence, the selectivity could be improved by repressing the dehydrogenating function of the metal. This was done by increasing the surface coverage with oxygen atoms or by filling the metal *d*-orbitals with electrons from Au. In this connection, note that alloying Au had the same effect as raising the O_2 pressure on the pressure of C_2H_4 required for maximum rate (compare Figs. 5, 7, and 10). Both increase this pressure.

In the formation of acetic acid from ethylene, if the transfer of hydrogen from one carbon to the other (to form the methyl group) is via the catalyst surface, then the methyl groups should contain d_0 and d_1 (and d_2 and d_3) in approximately equal amounts when C_2H_4 and C_2D_4 are cooxidized. The data (Table 3) show that this is not the case. In fact, the distribution is about that expected from the isotope scrambling in the ethylenes when account is taken of the fact that only part of these reactant gases may have been chemisorbed. Hence, the hydrogen transfer probably is intramolecular. This is exactly what happens when the same reaction is catalyzed by Pd complexes in solution (*19*).

There should be no tendency for low temperature preparations of Pd–Au alloys to form separate surface phases, such as described for the Cu–Ni system (*7*, *8*). The linear increase in CO chemisorption with Pd content (Fig. 11) supports this contention. Although Trapnell (*20*) found that carbon monoxide chemisorbed on both Pd and Au, the heat of adsorption on the latter was small (8.7 kcal mole^{-1} and $\theta = 0.26$ at 63°). In the present work, CO did not appear to chemisorb on pure gold at 100° and it seems likely, therefore, that chemisorption on the alloys occurred on individual Pd atoms in the surface. Our data, however, do not preclude the possibility of aggregates of Pd atoms existing as "islands" in the surface. The surface density of sites (atoms/cm^2) was calculated for each alloy using the equation of Brennan *et al.* (*16*). On this basis, the ratio of adsorbed CO molecules to surface Pd atoms was 0.6–0.7 for all the alloys and 0.6 for pure Pd. A 1:1 correspondence would not be expected because of the possibility of both bridged and linearly adsorbed species (*21*). The coverage found for pure Pd (8.1×10^{14} molecules cm^{-2}) was in good agreement with that found by Scholten and Van Montfort (*22*) for palladium sponge (8.6×10^{14} cm^{-2}) and by Stephens (*23*)* for evaporated films (8.9×10^{14} cm^{-2}).

The chemisorption of O_2 on the alloys (Fig. 12) followed a pattern considerably different from that found for carbon monoxide. The coverage was a maximum for 20% Pd–Au, a minimum for the 50% alloy and was high for pure Pd. Stephens (*23b*) studied the chemisorption of O_2 on evaporated Pd and Pd–Au alloy films and found that chemisorption took place in two stages: a fast initial uptake, accounting for ½ or more of the total, followed by a

* The surface coverage was taken from Ref. (*23a*) and the surface area from (*23b*).

slower adsorption process which eventually resulted in a total of about 1 oxygen atom/surface atom. It was suggested that the two processes corresponded to chemisorption on surface Pd atoms followed by slow diffusion to less active sites (Au) which were unable to adsorb oxygen directly. With regard to the fast and slow oxygen uptakes, our results agree qualitatively with those of Stephens, but quantitatively, the O_2 coverages were much smaller than a monolayer in the present work. In fact, by assuming oxygen was adsorbed as atoms and that CO measured the Pd monolayer capacity, fractional surface coverages near unity were found only for pure Pd and the 80% Au alloy (Fig. 12).

There was a striking similarity between the normalized fast oxygen chemisorption curve (Fig. 12) and the selectivity-composition relationship (Fig. 9). The fundamental reasons for this are obscure, but the observation seems consistent with the increase in selectivity with O_2 pressure. The excess enthalpy of formation goes through a similar minimum near 40% Pd (*6*) and the maximum deviation from Vegard's law occurs at about 30%. It is possible that a kind of short-range order exists in this region leading to special properties. On the other hand, in this composition range, a large fraction of the surface Pd atoms may not have adjacent Pd atoms. Isolated Pd atoms might be able to attack the C_2H_4 molecule at only one end, leading to higher selectivity. The ability of the 20% Pd–Au alloy to oxidize acetaldehyde to acetic acid was apparently low, because substantial amounts of the former were formed. It is possible that alloys of this composition have unusually high selectivities for other oxidation reactions, because such a catalyst has been used for oxidative dehydrogenation of butenes to butadiene (*24*).

The Pd–Au alloys showed a variation in catalytic activity (Fig. 8) similar to that found for CO oxidation over Pd–Au (*25*) and for ethylene oxidation in the presence of Pd–Ag (*18*). The rapid fall in activity from pure palladium to a constant plateau in the composition range 20–80% Pd is apparently characteristic of oxidation reactions over these alloy systems. Both Daglish and Eley (*25*) and Moss and Thomas (*18*) attributed the lower activity of the alloys to a filling of the *d*-levels of the palladium with a consequent reduction in their ability to chemisorb oxygen. It is difficult to see, however, how this picture could predict a plateau of constant activity. Nevertheless, in a later paper (*10*), we show that the relative activities of Group VIII noble metals are consistent with the importance of vacant *d*-orbitals in chemisorbing oxygen and are inconsistent with the operation of geometric effects in these systems.

Before concluding, it is of interest to point out the effect of sodium and boron impurities in Pd and Pd–Au alloys prepared by reduction with sodium borohydride. In the oxidation of ethylene over these materials, the rates were 10^{-1} to 10^{-2} times as fast as observed with samples prepared by reduction with hydrazine. In addition, the initial selectivities were markedly decreased, e.g., to less than 20% for pure Pd and to only 4% for an alloy containing 24% Pd. Apparently, the ability to chemisorb oxygen had been greatly diminished by impurities. One measurement was made to illustrate this point; the surface coverage by oxygen on the 24% alloy (Method II) after 95 min at 100° was 0.14×10^{14} molecules cm^{-2} or only one quarter that found for the 20 or 30% alloys prepared by Method I. In contrast, the carbon monoxide chemisorption gave almost identical coverages with both samples.

Acknowledgment

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

References

1. Lefort, T. E., *U. S. Pat.* 1,998,878 (1935).
2. Kemball, C., and Patterson, W. R., *Proc. Roy. Soc. (London), Ser.* **A270**, 219 (1962).
3. Gerberich, H. R., and Hall, W. K., *Nature* **213**, 1120 (1967).
4. Flank, W. H., and Beachell, H. C., *J. Catalysis* **8**, 316 (1967).

5. MAELAND, A., AND FLANAGAN, T. B., *Can. J. Phys.* **42**, 2364 (1964).
6. DARBY, J. B., *Acta Met.* **14**, 265 (1966); *Ind. Eng. Chem.* **60**(5) 29 (1968).
7. SACHTLER, W. M. H., AND DORGELO, G. J. H., *J. Catalysis* **4**, 654 (1965).
8. SACHTLER, W. M. H., AND JONGEPIER, R., *J. Catalysis* **4**, 665 (1965).
9. HANSEN, M., "Constitution of Binary Alloys," p. 224f. McGraw-Hill, New York, 1958.
10. CANT, N. W., AND HALL, W. K., *J. Catalysis* **16, 220 (1970).**
11. HIGHTOWER, J. W., GERBERICH, H. R., AND HALL, W. K., *J. Catalysis* **7**, 57 (1967).
12. KULIFAY, S. M., *J. Am. Chem. Soc.* **82**, 4916 (1961).
13. MCKEE, D. W., *J. Phys. Chem.* **70**, 525 (1966).
14. MELANDER, L. C., "Isotope Effects on Reaction Rates," Ronald Press, New York, 1960.
15. BADDOUR, R. F., MODELL, M., AND HEUSSER, U. K., *J. Phys. Chem.* **72**, 3621 (1968).
16. BRENNAN, D., HAYWARD, D. O., AND TRAPNELL, B. M. W., *Proc. Roy. Soc. (London), Ser. A* **256**, 81 (1960).
17. BEECK, O., Discussions Faraday Soc. **8**, 118 (1950).
18. MOSS, R. L., AND THOMAS, D. H., *J. Catalysis* **8**, 162 (1967).
19. STERN, E. W., *Catalysis Rev.* **1**, 73 (1967).
20. TRAPNELL, B. M. W., *Proc. Roy. Soc. (London), A* **218**, 566 (1953).
21. EISCHENS, R. P., FRANCIS, S. A., AND PLISKIN, W. A. *J. Phys. Chem.* **60**, 194 (1956).
22. SCHOLTEN, J. J. F., AND VAN MONTFOORT, A., *J. Catalysis* **1**, 85 (1962).
23. STEPHENS, S. J., (a) *J. Phys. Chem.* **63**, 188 (1959); (b) *Natl. Symp. Vacuum Technol. Trans.* **4, 34 (1957).**
24. ARMSTRONG, W. E., *U. S. Pat.* 3,156,735 (1964).
25. DAGLISH, A. G., AND ELEY, D. D., *Actes Congr. Intern. Catalyse, 2e, Paris, 1960* **2**, 1615 (1961).