The Catalytic Oxidation of Olefins on Metal Films

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The catalytic oxidation of a series of acyclic olefins has been studied on evaporated films of palladium and platinum using a mass spectrometer to analyze the products which, in some cases, were confirmed by gas chromatography. The main reaction in all cases was complete oxidation to carbon dioxide and water, but small amounts of acetone were produced by side reactions in the oxidation of propylene and higher olefins and more substantial amounts of *tert*-butyl methyl ketone were formed from *tert*-butylethylene over palladium.

Activation energies and frequency factors were determined over the temperature range from 50° to 130°C for reaction of a number of methyl-substituted ethylenes over both metals. Approximately first order dependence on olefin pressure was observed over palladium but different kinetics were found with platinum on which there was zero order dependence on olefin and, in the case of propylene, the rate of reaction varied with the half power of the oxygen pressure.

The oxidation of ethylene on platinum took place over the temperature range from 5° to 100°C and the results obtained were similar to those reported previously for palladium (*1*).

Oxidative dehydrogenation of cyclohexene to benzene was studied over palladium in the range of temperature from −20° to 30°C and the complete oxidation of benzene occurred at temperatures above 50°C.

A few experiments with ethylene and propylene were carried out over films of rhodium, gold, and tungsten and these indicated that the strength of the metal–oxygen bond is an important factor governing the relative activity of the metals as oxidation catalysts. The effect of the presence of hydrogen chloride on the activity of palladium films was also examined.

INTRODUCTION

Due to the likely occurrence of complete oxidation to carbon dioxide and water, comparatively few studies have been carried out on the catalytic oxidation of olefins on metals such as platinum, palladium, and rhodium which are resistant to bulk oxidation at low temperatures. Some investigations have been carried out on the oxidation of propylene and higher olefins on silver and on transition metal oxides and the more important of these have been reviewed recently by Dixon and Longfield (*2*). A recent investigation (*1*) showed that in the oxidation of ethylene on palladium films, carbon dioxide and water were the main products of the reaction in the temperature range 50° to 140°C and that the reaction was progres-

sively poisoned by small amounts of acetic anhydride and acetic acid formed in a side reaction. The oxidation of acetaldehyde on palladium resulted in the formation of acetic anhydride in almost quantitative yield and it was suggested that, in the oxidation of ethylene, acetaldehyde was a possible primary product leading to the formation of acetic anhydride and, by hydrolysis of the latter, acetic acid.

The first object of the present work was to compare the oxidation of methyl-substituted ethylenes with the results obtained previously for ethylene on palladium films, in order to examine the influence of the steric or electronic effects of the side groups on the ease of oxidation of the olefins and on the tendency to form products involving only

partial oxidation. The second object was to compare results on other metal films with those for palladium. The metals selected for study were platinum, rhodium, gold, and tungsten. Preliminary investigation showed that platinum was much more active as an oxidation catalyst than the last three metals and consequently it was used with a much wider range of olefins than were rhodium, gold, and tungsten.

Butyagin and Elovich (3) and Butyagin and Margolis (4) studied the oxidation of propylene on a platinum on barium sulfate catalyst. Carbon dioxide and water were the only products obtained and it was suggested that gas-phase propylene formed a complex with adsorbed oxygen which was further oxidized on the surface at temperatures lower than 80°C. At higher temperatures unstable peroxides were believed to desorb from the surface and carry the oxidation process into the gas phase.

EXPERIMENTAL

The reactions were studied in a static system on evaporated films and followed by means of a Metropolitan-Vickers MS2 mass spectrometer, the ion source of which was connected to the reaction vessel by a fine capillary leak. The main features of the apparatus and of the preparation of evaporated metal films have been previously described (5).

The preparation of ethylene and oxygen have been described in a previous paper (1). Propylene and isobutene were prepared by the dehydration of isopropyl and tert-butyl alcohols over activated alumina at 300–350°C, and trimethylethylene, by the dehydration of tert-amyl alcohol in 33% w/v sulfuric acid at 50°C. Tetramethylethylene of 96% purity was obtained from K and K Laboratories, Inc., New York. Propylene and isobutene were purified by repeated distillation from liquid nitrogen traps and tri- and tetramethylethylene by preparative gas chromatographic techniques. Finally, all olefins were thoroughly degassed by repeated freezing in liquid nitrogen and pumping, and checked for purity of not less than 99% mass-spectrometrically. Palladium and platinum films were evaporated from wires (0.2

and 0.1 mm diameter, respectively) of spectrographically standardized grade supplied by Johnson, Matthey and Co., Ltd., and these were wound on 0.3 mm diameter tungsten filaments.

The standard reaction mixture for use with olefins lighter than, and including, isobutene consisted of 2.3 ± 0.1 mm of olefin and 24 mm of oxygen admitted to a freshly prepared film in the reaction vessel (196 ml capacity) at 0°C, which was then heated rapidly to the required temperature by means of an electric furnace. Under these conditions, the vessel contained 1.56×10^{19} molecules of olefin before reaction. For reactions involving tri- and tetramethylethylene 1.1 mm olefin was used for making up the mixture. Only one reaction was usually carried out on each film but occasionally it was possible to follow a reaction on a particular film at a second higher temperature after sufficient information had been obtained at the lower temperature.

All mass spectrometric analyses were carried out with the use of 25 volt electrons to ionize the molecules. Carbon dioxide and acetone were estimated by the parent ions of mass 44 and the fragment ion of mass 43, respectively. Fragment ions, used to estimate the other olefins, were as follows: mass 26 for ethylene, 41 for propylene, isobutene, and tetramethylene, and 55 for trimethylethylene. Calibration with suitable mixtures gave the relative sensitivities for the different reactants and products.

The difficulties encountered in the mass spectrometric analysis of mixtures containing oxygen and the use of argon as an internal standard have been described previously (1). In the present work krypton was also used on those occasions when the interference of other peaks of mass 40 made it impossible to use argon.

As the work proceeded, the importance of confirming the presence or absence of small quantities of partial oxidation products became apparent so the procedure was adopted whereby the products from several experiments were collected by freezing in liquid nitrogen and subsequently expanded through the capillary leak into the mass spectrometer from a bulb of small volume.

In this way more clearly defined spectra were obtained and the limit of detection of the mass spectrometer increased by factors of 10 to 20. Further analysis of the combined product was carried out using a Pye Argon Chromatograph with a 4-ft column containing 10% by weight of polyethylene glycol (molecular weight 200) dispersed on Celite (85–100 B.S.S. mesh) and operated at room temperature.

RESULTS

The oxidation of ethylene on platinum films. The oxidation of ethylene on platinum films occurred at conveniently measurable rates in the temperature range 5–100°C. Carbon dioxide and water were the only products of the reaction and, based on the amounts of ethylene and carbon dioxide, the total carbon in the gas phase remained close to 100%. A typical result is shown in Fig. 1. An activation energy of 11.7 kcal/mole was derived from the Arrhenius plot for the initial rates of reaction expressed as per cent oxidized/min 100 cm² of apparent

surface area of the films. More consistten results were obtained when the activity was related to the apparent geometric areas rather than the weights of the films, possibly due to substantial sintering of the films on admission of the reaction mixture. The absolute initial rate of reaction, expressed as molecules of ethylene reacting per second per square centimeter of apparent surface was given by

$$r_0 = 10^{21.7 \pm 0.9} \exp\left(-11700 \pm 1100/RT\right)$$

for the standard mixture.

It was believed that, in excess oxygen, the reaction would follow simple kinetic dependence on the pressure of ethylene, but attempts to describe the course of the reaction in terms of first or zero order kinetics failed, as is shown by the appropriate plots in Fig. 1. A progressive falloff in rate occurred at all temperatures except at 100°C when, after an initial decrease, the rate remained more or less constant before finally accelerating during the last 20% reaction. It was apparent that the progressive poisoning of the reaction
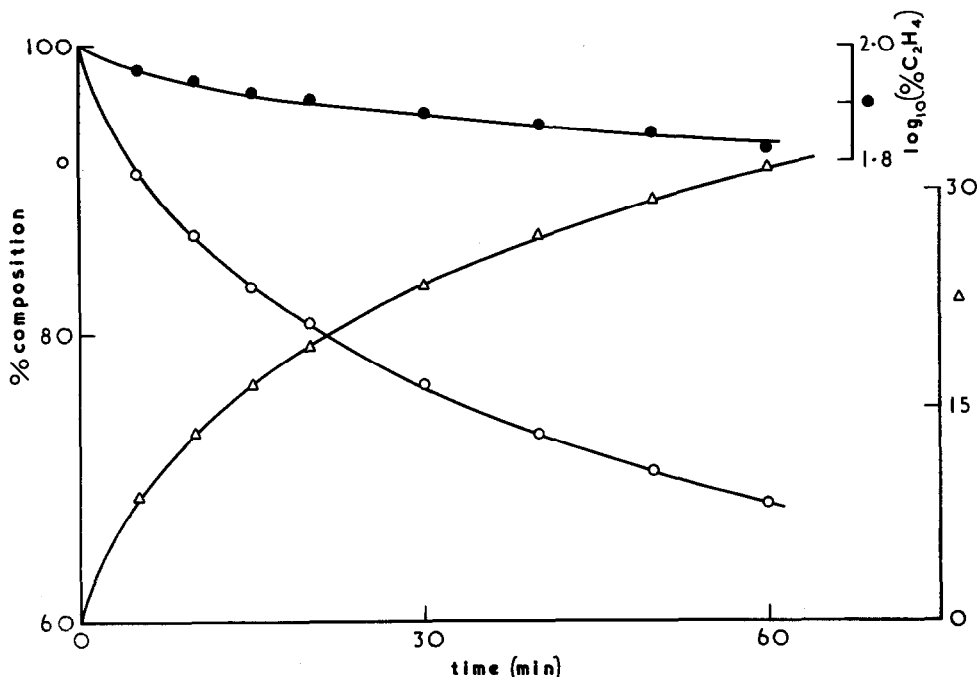

FIG. 1. A typical result for the oxidation of ethylene on platinum at 50°C. Analysis is based on the carbon content of the compounds present: ◯, ethylene; △, carbon dioxide; and ●, the corresponding first order plot.

was similar to that observed on palladium and, on the assumption that small amounts of acetic anhydride or acetic acid not detectable in the gas phase could be responsible for the poisoning of platinum, the effect of including acetic acid in reaction mixtures was investigated. The inclusion of 0.6 mm acetic acid in the standard reaction mixture on platinum at 79°C reduced the initial rate by a factor of 18. After an initial decrease, the rate of the reaction was constant (Fig. 2), showing that the influence of the added acetic acid was large compared with the poisoning normally associated with the progress of the reaction.

Some experiments were carried out to determine the reactivity of ethane towards oxidation on platinum. A standard mixture of ethane and oxygen at 305°C gave carbon dioxide and water as the only products at an initial rate of 1.6%/min 100 cm², i.e. 6×10^3 times more slowly than the extrapolated rate for ethylene at the same temperature. Subsequently, the rate of reaction was proportional to the pressure of ethane.

The oxidation of methyl-substituted ethylenes. The oxidation of propylene and isobutene occurred at conveniently measurable rates on platinum and palladium films in the temperature range 50–130°C and tri- and tetramethylethylene on platinum in the same temperature range. In all cases, carbon dioxide and water were the major products of reaction, although small amounts of acetone were also formed in yields not exceeding 8%. Based on the amounts of olefin, carbon
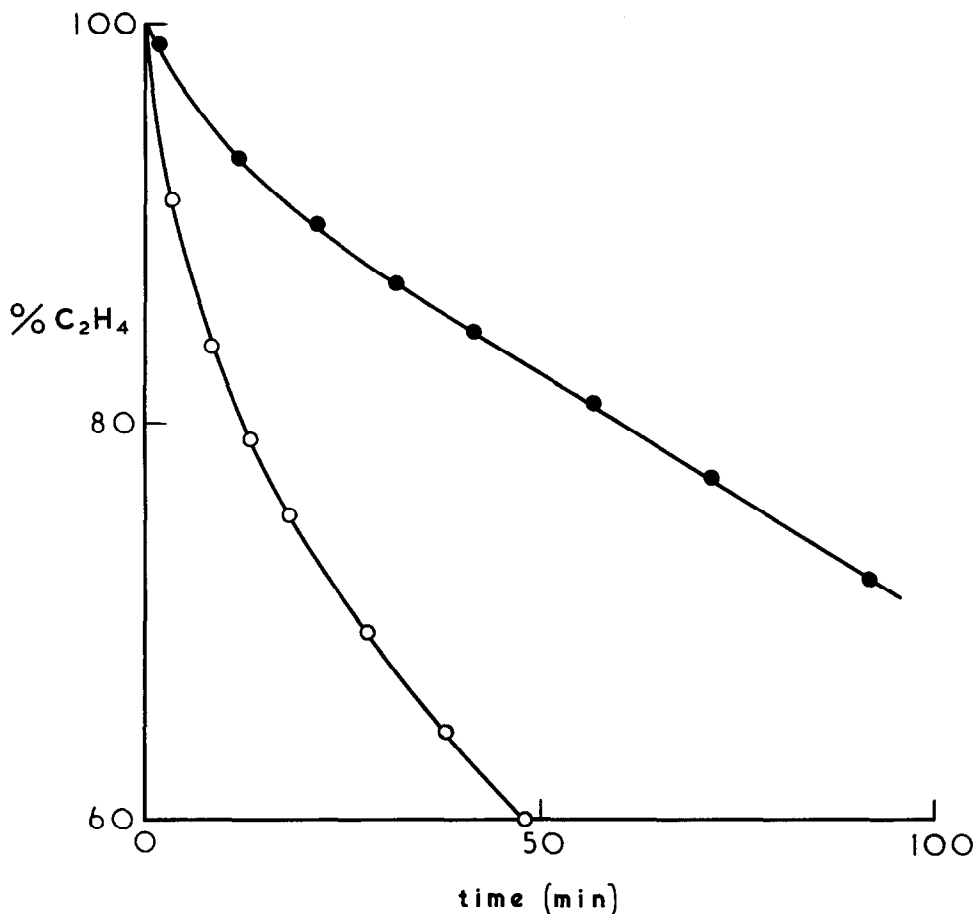

FIG. 2. The effect of added acetic acid on the oxidation of ethylene on platinum: ○, a normal reaction at 65°C; and ●, a reaction with added acetic acid at 79°C.

dioxide, and acetone, the total carbon in the gas phase remained close to 100%, and a typical result is shown in Fig. 3. On plati-

also eliminated any effect of a sharp decrease in the rate of oxidation which was sometimes observed in the first few minutes for reac-
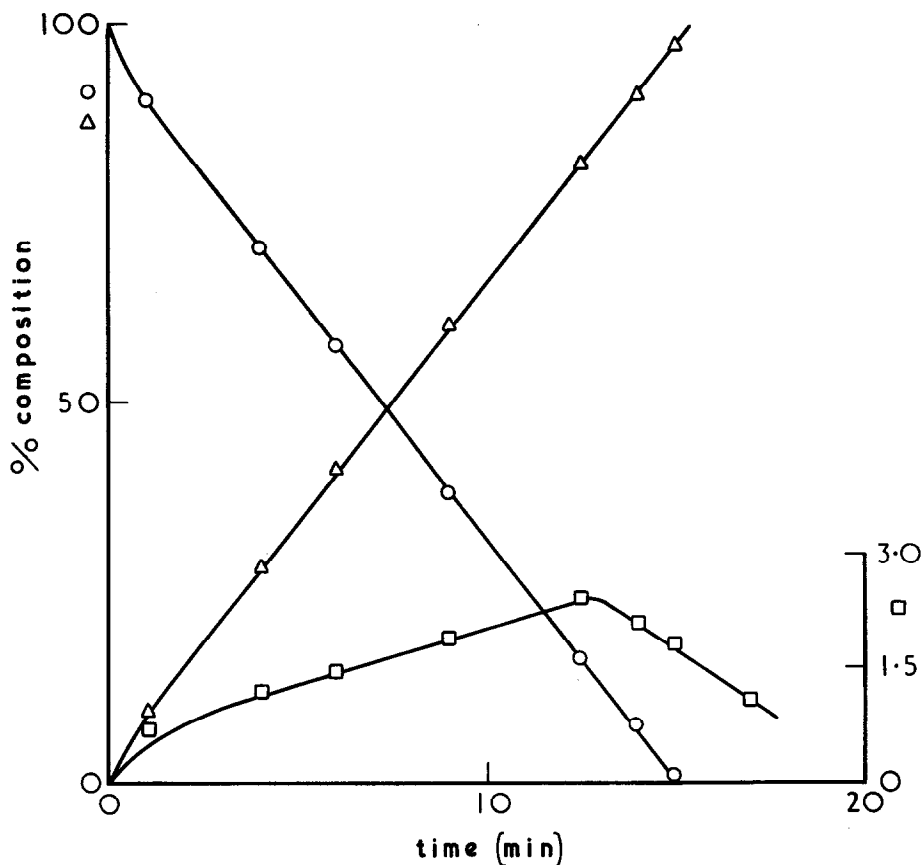

FIG. 3. The oxidation of trimethylethylene on platinum at 100°C; $\bigcirc$, trimethylethylene; $\triangle$, carbon dioxide; and $\square$, acetone.

num, the rates of oxidation of isobutene, tri-, and tetramethylethylenes were similar but the corresponding rate for propylene was lower than those of the other olefins by factors ranging from 2 at lower temperatures to 6 at higher temperatures.

In all cases where the course of the reactions followed well-defined kinetics the rates were expressed as "kinetic" initial rates derived from the rate constants of the appropriate kinetic plots. More accurate results were obtained in this way than by the direct measurement of the initial rate because any uncertainty about the time at which the reaction vessel reached the desired temperature was eliminated. The procedure

tions at low temperatures and which was thought to be caused by completion of a sintering process. Satisfactory Arrhenius plots were obtained for the formation of carbon dioxide, expressed as %/min 100 cm^2 of geometric film area; some typical examples are shown in Fig. 4. The derived activation energies and the frequency factors in absolute units for the formation of carbon dioxide and, in some cases, acetone are given in Table 1 for platinum and Table 2 for palladium. These tables also include data on the maximum percentages of acetone formed from the various olefins. Isolated experiments with tetramethylethylene on palladium at 115° and 140°C gave initial
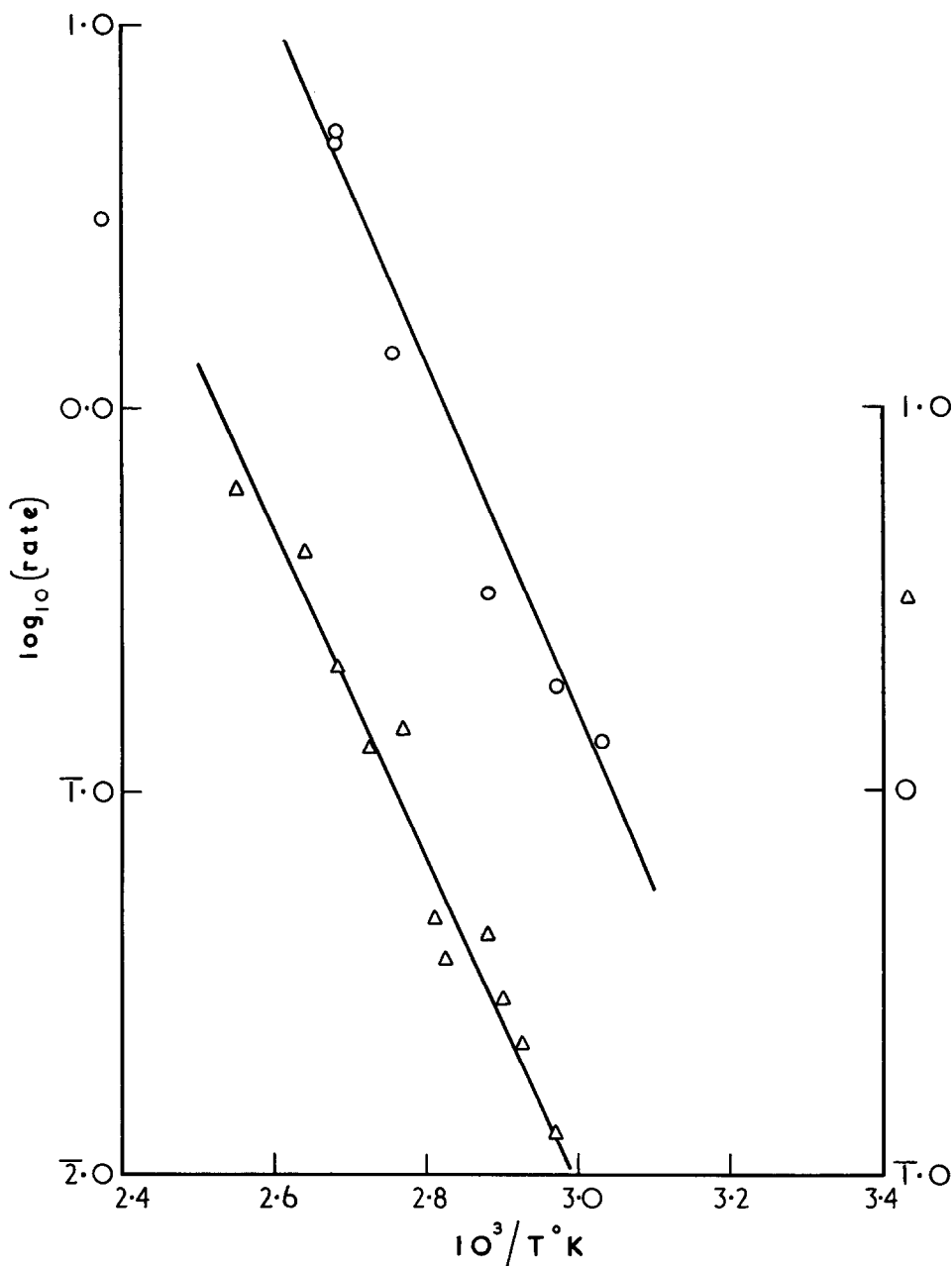
FIG. 4. Typical Arrhenius plots for the formation of carbon dioxide and water in the oxidation of methyl-substituted ethylenes on platinum. Rates are expressed as % oxidized/min 100 cm²: ◯, trimethylethylene; and △, tetramethylethylene.

rates of oxidation of 3.2 and 25%/min 100 cm² with maximum percentages of acetone of about 7%. The activation energy for the formation of carbon dioxide based on these two experiments was 21 kcal/mole.

There was evidence that the oxidation of acetone was retarded by the presence of olefin and this is shown by the typical results in Fig. 3. This effect was confirmed by including 1.2 mm of acetone in a standard

TABLE 1

ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR OXIDATIONS ON PLATINUM

Olefin	Temp. range (°C)	Maximum yield of acetone (%)	Formation of carbon dioxide		Formation of acetone	
			E' (kcal/mole)	$\log_{10} A'^a$	E'' (kcal/mole)	$\log_{10} A''^a$
Propylene	76–130	~1	17.0 ± 0.7	23.1 ± 0.5	—	—
Isobutene	61–115	3–5	21.4 ± 1.5	26.1 ± 0.9	28.9 ± 2.1	29.1 ± 1.3
Trimethylethylene	57–100	3–5	21.6 ± 2.3	26.4 ± 1.5	20.7 ± 2.6	24.4 ± 1.6
Tetramethylethylene	64–119	3–8	20.2 ± 1.3	25.3 ± 0.8	14.1 ± 2.0	20.3 ± 1.3

[a] A in molecules of olefin reacting/sec cm² of catalyst.

TABLE 2

ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR OXIDATIONS ON PALLADIUM

Olefin	Temp. range (°C)	Maximum yield of acetone (%)	Formation of carbon dioxide		Formation of acetone	
			E' (kcal/mole)	$\log_{10} A'^a$	E'' (kcal/mole)	$\log_{10} A''^a$
Propylene	84–128	~3	20.8 ± 1.3	25.4 ± 0.8	—	—
Isobutene	83–125	3–5	22.6 ± 0.8	26.5 ± 0.5	24.3 ± 2.0	26.2 ± 1.2

[a] A in molecules of olefin reacting/sec cm² of catalyst.

mixture of isobutene and oxygen and carrying out an oxidation on palladium at 87°C; the oxidation of the olefin took place at the normal rate but no oxidation of acetone occurred until most of the olefin had been destroyed.

Detailed kinetic studies were carried out on the oxidation of propylene on platinum. Results for a series of experiments with varying pressures of propylene and a fixed pressure of 24 mm of oxygen, given in Table 3, indicated an order of reaction of about

TABLE 3

THE INFLUENCE OF PROPYLENE PRESSURE ON THE "KINETIC" INITIAL RATE OF REACTION ON PLATINUM AT 107°C WITH A FIXED PRESSURE OF OXYGEN OF 24 MM

Propylene pressure (mm)	1.2	2.2	2.4	4.6	7.6
Rate (%/min 100 cm²)	2.65	1.16	1.45	0.53	0.33
Pressure × rate	3.18	2.55	3.48	2.44	2.50

−0.2 with respect to the pressure of propylene. A second series of experiments with a fixed pressure of propylene and varying pressures of oxygen is reported in Table 4

TABLE 4

THE INFLUENCE OF OXYGEN PRESSURE ON THE OBSERVED INITIAL RATE OF REACTION ON PLATINUM AT 107°C, WITH A FIXED PRESSURE OF PROPYLENE OF 2.4 MM

Oxygen pressure (mm)	6.8	26	44	60
Rate (%/min 100 cm²)	0.58	1.11	1.94	2.20
Rate/(pressure)$^{\frac{1}{2}}$	0.272	0.218	0.293	0.284

and Fig. 5. The initial rates of these reactions had to be measured directly and were not obtained from kinetic plots because of the variations and complexity of the kinetic behavior of the experiments. The initial rates indicated an order of 0.5 to 0.6 with respect to the pressure of oxygen and the course of reaction A (see Fig. 5) with a low pressure of oxygen confirmed the half-order dependence on oxygen. Reaction B illustrates the behavior with the standard oxygen:propylene mixture of 10:1 and the constant rate of reaction may be explained by zero order dependence on the olefin pressure if any influence of the smaller percentage change in the oxygen pressure is ignored. Alternatively, the constant
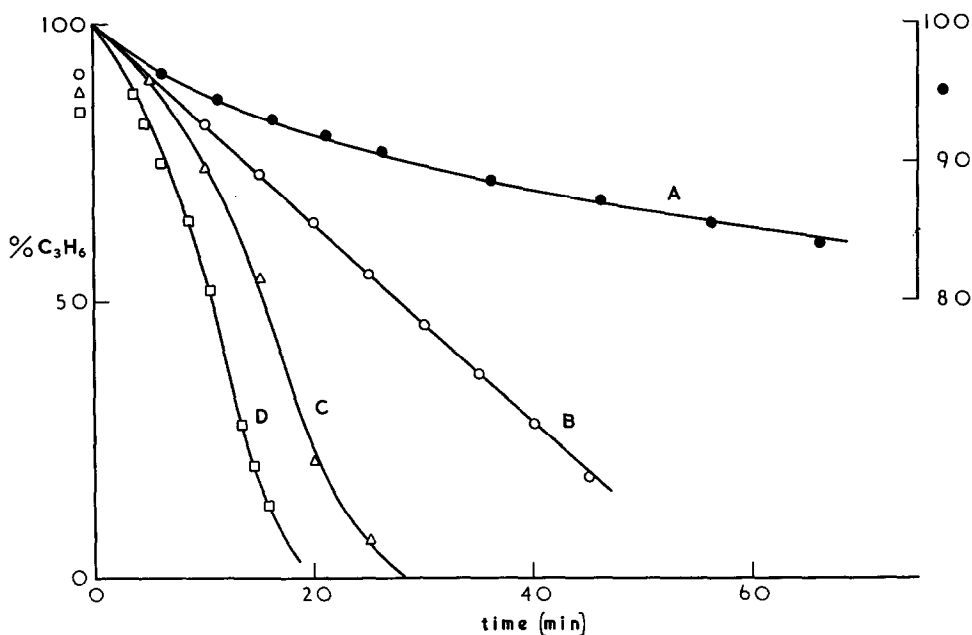
FIG. 5. Reaction of 2.4 mm of propylene with different pressures of oxygen on platinum at 107°C: A, 6.8 mm; B, 26 mm; C, 44 mm; and D, 60 mm.

rate may have resulted by chance from a combination of a slight negative order with respect to propylene together with a square root dependence on the pressure of oxygen. Reactions C and D, with the two highest pressures of oxygen, showed anomalous behavior with time. Any effect on the rate of reaction of the change in the oxygen pressure during the course of these reactions would not have been significant because of the large excess present; the sigmoid curves must be attributed to the influence of changes in the pressure of propylene and might be explained by an initial negative order with respect to this reactant changing to a positive order in later stages of the reaction.

The majority of the results, apart from the complications for experiments with a large excess of oxygen, conformed approximately to a zero order dependence on the pressure of propylene and a square root dependence on oxygen. It was assumed that similar kinetics were obeyed with standard mixtures of the other substituted ethylenes on platinum as constant rates of reaction, cf. Fig. 3, were observed except during the

last 10% of reaction, when the rate tended to increase with isobutene and decrease with tetramethylethylene. Detailed pressure dependence experiments were not carried out on palladium but the course of reactions with the standard mixtures showed apparent first order behavior as illustrated in Fig. 6, except in the case of isobutene (and propylene) at higher temperatures, when the rate tended to become less dependent on olefin pressure after about 50 to 70% of reaction had occurred.

The oxidation of related compounds. Since the substitution of methyl groups in ethylene did not lead to any pronounced partial oxidation of the molecules, some experiments were carried out with *tert*-butylethylene, which has a quaternary carbon atom adjacent to the double bond. The total rate of oxidation of this compound at 160°C on palladium was about 30 times slower than the extrapolated rate for isobutene at this temperature. Partial oxidation occurred to form *tert*-butyl methyl ketone in addition to complete oxidation and the initial rates of formation of the ketone and carbon dioxide were 0.4 and
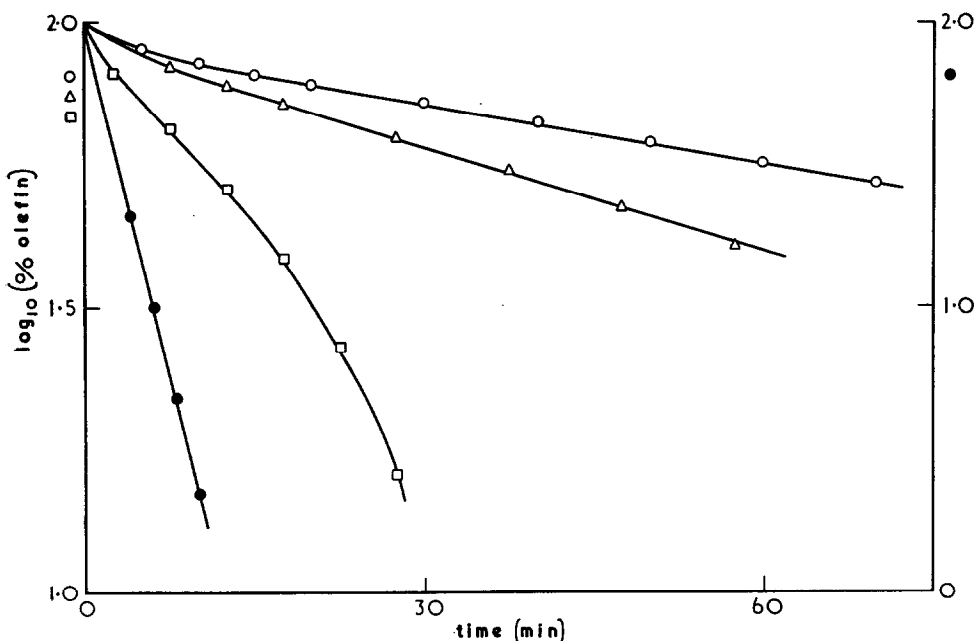
FIG. 6. First order plots for reaction on palladium: ◯, propylene at 105°C; △, isobutene at 107°C; ▢, isobutene at 124°C; and ●, tetramethylethylene at 140°C.

1.6%/min 100 cm², respectively. However, on platinum at 132°C, the oxidation of *tert*-butylethylene took place at an initial rate of 8.3%/min 100 cm², which was similar to rates for the methyl-substituted ethylenes; there was little selective partial oxidation, as a maximum of 2% of the ketone was formed during the course of the reaction.

Experiments were carried out to compare the rate of oxidation of a diene with the corresponding olefin. Complete oxidation of 1.1 mm of 2-methylbutadiene and 24 mm of oxygen took place on platinum at 87°C with an initial rate of 0.3%/min 100 cm², which was about ⅓th of the rate for trimethylethylene under similar conditions. Results with a mixture of equal pressures of 1.3 mm of the diene and the olefin and 24 mm of oxygen over palladium at 123°C are shown in Fig. 7. These show clearly that the oxidation of the olefin was inhibited significantly by the presence of the diene, which underwent preferential oxidation. The slower rate of oxidation of the olefin remained constant until the amount of diene was less than 10% and then accelerated sharply. Similar behavior was observed with a mixture of the two compounds on platinum at 116°C.

Some work was carried out on the oxidation of cyclohexene over palladium because we believed that benzene might be formed by oxidative dehydrogenation and appear as a product because it would undergo further oxidation less readily than the olefins. A mixture of 2.1 mm of cyclohexene and 24 mm of oxygen was allowed to react on palladium in the temperature range −20° to 30°C. No carbon dioxide was formed but a first order conversion of the cyclohexene to benzene was observed and small amounts of cyclohexane were also produced, as shown by the typical result in Fig. 8. The absolute rate of conversion of cyclohexene to benzene in a series of runs at increasing temperatures on a single palladium film was given by

$$r_c = 10^{25.6} \exp\left(-15,400/RT\right)$$

The oxidation of benzene to carbon dioxide and water was noticeable at temperatures greater than 50°C but cyclohexane remained resistant to oxidation until the temperature exceeded 250°C. In the absence of oxygen a rapid disproportionation of cyclohexene
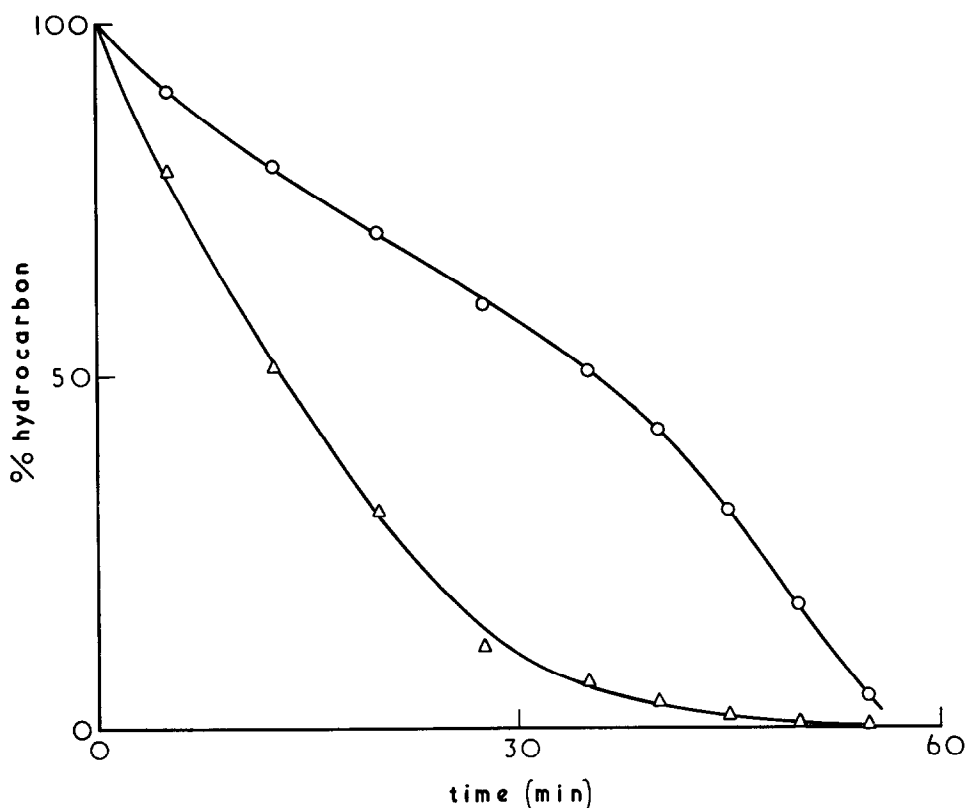
FIG. 7. The oxidation of a mixture of trimethylethylene and 2-methylbutadiene on palladium at 123°C; ○, trimethylethylene; and △, 2-methylbutadiene.

to cyclohexane and benzene occurred at 0°C on palladium, but similar experiments with trimethylethylene showed no disproportionation to the diene and the alkane even at temperatures of 400°C.

Reactions on rhodium, gold, and tungsten. A number of experiments were carried out on the oxidation of ethylene and propylene on these three metals in order to establish the relative activity of the metals as oxidation catalysts. In all cases, complete oxidation to carbon dioxide and water occurred but minute traces of acetone were formed from propylene on rhodium. Oxidation of both olefins occurred above 120°C on rhodium films and rates of 1.7%/min 100 cm² for ethylene at 155°C and 7.4 in the same units for propylene at 194°C were observed. Negligible oxidation of ethylene was found over gold films below 200°C but a slow reaction of propylene took place at 250° and the oxidation was completed in 12 hr. Very low

rates of oxidation of ethylene were found above 230°C on tungsten and 50% conversion of propylene to carbon dioxide and water occurred in 12 hr at 300°C.

The oxidation of ethylene on poisoned palladium films. The influence of hydrogen chloride as a poison for the oxidation of ethylene on palladium was studied in a number of ways to provide data for comparison with earlier results (1). Complete inhibition of reaction at temperatures up to 240°C was found when 1.2 mm of hydrogen chloride was included in a standard mixture of ethylene and oxygen. Admission of 0.9 mm to a film at 0°C, followed by pumping for 5 min, gave a catalyst of low activity on which reaction occurred slowly at 110°C. Neither of these experiments showed any significant difference from results with unpoisoned films (1) in relation to the proportions of acetic anhydride or acetic acid formed.
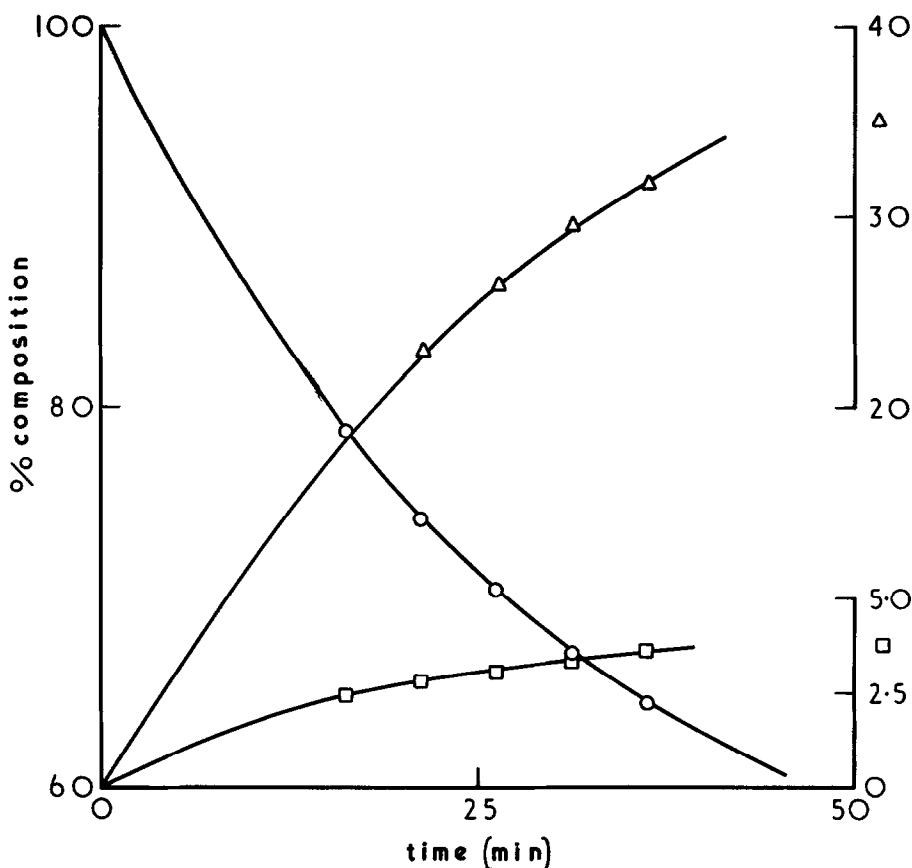
FIG. 8. The oxidation of cyclohexene on palladium at 0°C; O, cyclohexene; △, benzene; and □, cyclohexane.

A palladium film (12 mg) was prepared by evaporation in the presence of 0.2 mm of hydrogen chloride at 0° and then used for a reaction at 155°C. The initial rate of reaction was about ⅓th of that for a clean film but after all the ethylene had disappeared the products consisted of 85% carbon dioxide and 15% acetic acid, whereas clean films gave, at most, about 3% of acetic acid. Other films evaporated in hydrogen chloride were used to oxidize the four methyl-substituted ethylenes and *tert*-butylethylene; no significant change in product distributions were observed but in each case the rate of reaction was lower than over clean films. X-ray analysis of films evaporated in hydrogen chloride failed to reveal any lines other than those due to palladium but the films were found to have slight orientation with the

110 crystal faces parallel to the glass substrate.

DISCUSSION

The oxidation of ethylene on platinum takes place in a similar manner to the behavior already reported over palladium (1). Platinum is, however, a more active catalyst for the oxidation of ethylene than palladium and the difference in activity is attributable to the decrease in activation energy from 14.3 on palladium to 11.7 kcal/mole on platinum; the frequency factors over the two metals do not differ significantly. The partial oxidation of the ethylene to acetaldehyde, acetic anhydride, and acetic acid, which was shown to occur over palladium as a side reaction, cannot be as pronounced over platinum as none of

these products of partial oxidation were detected; however, the general form of the kinetics is similar over both metals and it is evident that acetic acid inhibits the oxidation of ethylene over both metals.

The data in Tables 1 and 2 show that, as in the case of ethylene, platinum is slightly more active than palladium for the oxidation of other olefins. If the results with rhodium, gold, and tungsten are taken into account as well, the relative activity for the oxidation of olefins of the five metals is given by

$$Pt > Pd > Rh >> Au > W$$
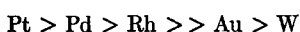
The order for the four transition metals may be correlated with data for the integral heats of adsorption of oxygen on evaporated films of each metal obtained by Brennan, Hayward, and Trapnell (6). The values they obtained were 67 kcal/mole for platinum and palladium, 76 for rhodium, and 180 for tungsten; thus the highest catalytic activity is found with the metals which adsorb oxygen least strongly. The low activity of gold cannot be explained by a strong adsorption of oxygen on the metal but is probably caused by the fact that the chemisorption of oxygen on gold does not occur readily, in contrast to the situation with the transition metals. Daglish and Eley (7) have suggested that the oxidation of carbon monoxide on gold wires may involve the activated adsorption of oxygen on special sites such as dislocation edges.

Ethylene is oxidized more readily than propylene on both platinum and palladium; the activation energies for the reaction of propylene are about 5 or 6 kcal/mole greater than those for ethylene, but in the case of palladium part of the increase in activation energy is counterbalanced by a 1000-fold increase in the frequency factor. There is little difference in the reactivity of propylene and of the other substituted ethylenes on both metals, although there is a further increase in activation energy as the size of the molecule is increased from C_3 to C_4 (Tables 1 and 2); however, there are compensating increases in the frequency factors as well.

Some of the information about the adsorp-tion of oxygen and of ethylene on transition metals is useful as a guide to the interpretation of the kinetic data for the oxidation of olefins on platinum and palladium. As the initial heats of adsorption of oxygen (6) on transition metal films are usually significantly greater than the corresponding heats of adsorption of ethylene (8), it is probable that oxygen will be more strongly adsorbed than olefins on clean metal surfaces. However, there must be a very marked decrease in the heat of adsorption with coverage on platinum and palladium because Brennan, Hayward, and Trapnell (6) found that only 63% of the surface of platinum and 74% of the surface of palladium was readily covered with oxygen. Data about the change of heat with coverage of olefins on platinum or palladium films are not available, but it is possible that olefin may be more strongly adsorbed on the final 30% of the surface of these metals than oxygen and this effect may be more marked with platinum than with palladium. These considerations may explain why the oxidation of ethylene on palladium showed a zero order dependence on oxygen pressure (1), but the oxidation of propylene on platinum gave a square root dependence. It is possible that, with the standard mixtures of propylene and oxygen on platinum, oxygen atoms are adsorbed in gaps between the adsorbed propylene molecules and so there is only, at most, a slight negative order of about −0.2 with respect to propylene. On the other hand, the larger negative order observed initially with experiments with higher pressures of oxygen may arise because the oxygen is competing for adsorption on sites which preferentially adsorb propylene.

We do not believe that the differences in the kinetic dependence on olefin pressure observed with platinum and palladium are connected with any fundamental difference in the mechanisms of the oxidations on the two catalysts. The zero order dependence with propylene and the higher olefins on platinum suggests that the olefins are more strongly adsorbed in the presence of oxygen on this metal than with the oxygen-palladium system, which exhibited first order dependence on olefin pressure. We believe

that a change from first order to zero order dependence would be found over palladium if higher pressures of olefin were used, as indeed was observed in the previous work on the oxidation of ethylene (*1*). It is not easy to decide whether the adsorbed olefin required in the rate-determining step is attached on top of an oxygen-covered surface or chemisorbed directly on the metal. The absence of any evidence for inhibition of reaction by oxygen would favor the first of these alternatives but we cannot exclude the possibility that the oxidation is occurring on the fraction of the surface on which oxygen is not very strongly adsorbed. The general conclusion from the kinetic data is that the rate-determining step involves an adsorbed olefin molecule, possibly on top of an oxygen-covered surface and a chemisorbed oxygen atom.

The acetone which was formed to a small extent in the oxidation of a number of olefins on both platinum and palladium cannot be an intermediate in the complete oxidation but must arise through a side reaction, just as in the case of the acetic anhydride and acetic acid formed from the oxidation of ethylene on palladium (*1*). This point is clearly established by the evidence that the presence of olefins inhibits the oxidation of acetone and by the absence of any induction period for the formation of carbon dioxide from the olefins. All olefins containing three or more adjacent nonquaternary carbon atoms gave similar amounts of acetone and there was no enhanced production of this ketone by selective oxidation of the double bond in molecules like isobutene, trimethylethylene, or tetramethylethylene. Since acetone could be formed without the rupture of a carbon–carbon bond from propylene, the absence of large amounts of the ketone in the oxidation of propylene suggests that the rupture of carbon–carbon bonds must occur fairly readily under oxidative conditions on both metals. It is interesting that the amounts of acetone formed from most olefins were similar even though there was a large variation in the activation energy for the reaction, as may be seen in Table 1.

The only case where the structure of one of the acyclic olefins gave rise to increased amounts of partial oxidation products was the reaction of *tert*-butylethylene on palladium. The relatively high amount of *tert*-butyl methyl ketone produced is evidence for enhanced stability of a structure with a quaternary carbon atom adjacent to the double bond under oxidative conditions. This suggests that a possible mode of attack of oxygen on the olefins may involve removal of allylic hydrogen atoms. The absence of any isopropyl methyl ketone from trimethylethylene is an indication that ketones containing the same number of carbon atoms as the olefin are only formed if there are hydrogen atoms on both the doubly-bonded carbon atoms.

The occurrence of oxidative dehydrogenation with cyclohexene on palladium and the absence of any analogous reaction to yield 2-methylbutadiene from trimethylethylene, which is also feasible thermodynamically, are interesting. An important factor will be the strength of adsorption of the dehydrogenated compound relative to that of the original olefin. In other words, some diene may be formed on the surface of the catalyst in the oxidation of trimethylethylene but it may be too strongly adsorbed to appear as a product. A second factor will be the relative rates of oxidation and desorption of the dehydrogenated compound. The low rate of oxidation of benzene is obviously important in relation to the behavior observed with cyclohexene. Apart from this special case, it is clear that the complete oxidation of the olefins will not, in general, take place through dienes as intermediates, as shown by the experiments on the relative rates of oxidation of 2-methylbutadiene and trimethylethylene.

The absence of any inhibition of oxidation by carbon dioxide and water and the more rapid production of these compounds from ethylene than from the other olefins indicate that the desorption of these products cannot be the rate-determining step in the oxidation of olefins. The extremely slow oxidation of alkanes relative to the rates for the corresponding olefins suggests that the initial adsorption of the alkane is rate-determining. This provides some further confirmation that oxidation probably occurs by adsorp-

tion on top of an oxygen-covered surface, since the adsorption of alkanes on portions of metal free of oxygen would not be likely to require temperatures of over 200°C. In this connection, it is relevant to note that the presence of oxygen did not poison substantially the exchange of n-hexane with deuterium on palladium (9).

The work with palladium films subjected to treatment in different ways with hydrogen chloride was undertaken because Smidt (10) has shown that palladium catalysts prepared by reduction of palladous chloride were active in the oxidation of ethylene to acetaldehyde. Our results confirm that the films prepared in hydrogen chloride show more tendency for selective oxidation of ethylene than clean films, but the effects are not marked.

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