THE ELECTROCHEMICAL OXIDATION OF HYDROCARBONS; NATURE AND ACTIVITY OF ELECTRODEPOSITED PLATINUM BLACKS CONTAINING VARYING AMOUNTS OF LEAD

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INTRODUCTION

The electrochemical oxidation of hydrocarbons, such as propane, at relatively high rates necessitates the use of a finely divided platinum catalyst.[1-5] Other materials that have been tried, namely, palladium,[6-9] nickel,[6] silver,[9] cobalt molybdate,[10] and nickel boride,[11] although showing some activity, are not as satisfactory. In a recent paper[12] it was indicated that high rates of oxidation can be sustained only if large amounts of platinum (>35 mg./cm.^{2}) are used. Smaller amounts (9 mg./cm.^{2}) do not perform quite as well. A question that immediately arises is whether surface area is the sole criterion for electrochemical activity. From the experimental fact that electrodes containing the same amount of platinum have a variable activity, it might be suggested that there is some other important physical property playing a significant role.

At this time, only a few attempts have been made to investigate the role of the catalyst in organic electro-oxidation.[13, 14] Dahms and Bockris[14] made a comparative study of the anodic oxidation of ethylene on bright metal electrodes made of Au, Ir, Pd, Pt, and Rh in M sulfuric acid at 80° C. No attempt appears to have been made to determine the reasons for the catalytic activity of the finely divided metals, particularly of platinum. Joncich and Hackerman[15] have studied the relationship between the surface area of electrodeposited platinum black and concentration of chloroplatinic acid plating solution, current density, time, and geometry of the electrode system. Among other things, they showed that for a particular solution and system there is an optimum current density which gives the maximum surface area. In an earlier paper, Bianchi[16] showed that the character of electrodeposited platinum black can be profoundly altered by the inclusion of heavy metal ions in the plating solution. Pb, Hg, Cd, and Tl inclusions in the deposit led to an increase in the lattice parameter, whereas Cr, Mn, Fe, Co, Ni, Cu, Zn, and Pd led to a decrease. Sb, Bi, Sn, As, and Au, although altering the appearance of the deposit, had no effect on the lattice parameter.

Since a hydrocarbon electrode reaction involves an initial adsorption step, it would appear that the lattice spacing of the catalyst is important. By using electrodeposited platinum black containing various inclusions, it is possible that some indication of the effect of lattice spacing in electro-organic reactions might be obtained.

The work reported here consists of an investigation of the effect of lead content on the nature of electrodeposited platinum, and the activity of these deposits toward the electrochemical oxidation of ethane, ethylene, propane, propylene, and n-butane in 5M H_3PO_4 at 80° C.

EXPERIMENTAL

The cell used in this work is shown in Fig. 1 (a). It consisted of a Pyrex glass tube, 12 cm. long and 3.5 cm. in diameter, with a coarse glass frit, H, sealed into it, 2 cm. from the bottom. Two glass tubes, A and B, 8 mm. outside diameter, each having a 7/25 socket sealed to the ends, were connected to the cell, one below the frit and the other 2 cm. from the top. These tubes were used for admitting and venting gases, as indicated in the figure. The cell top contained four 7/25 sockets

which supported three working electrodes, F, and a reference electrode, C. The working electrodes consisted of a platinum wire, 1 cm. long and 0.5 mm. in diameter, sealed through a 7-cm. long tube, which was connected to a 7/25 through-cone. The reference electrode, a Beckman saturated calomel electrode with a fiber junction, was connected to the cell through a salt bridge containing the same electrolyte. The salt bridge was comprised of a 7/25 through-cone and a closed, electrolyte-lubricated stopcock, D. The tip of the bridge tube was drawn down and then bent up to prevent gas bubbles from getting into it. The counterelectrode, G, consisted of a close fitting, 2-cm. long platinum gauze (50 mesh) cylinder. A platinum lead connected to this electrode was sealed through a small side tube at the upper end of the cell. About 40 cc. of electrolyte was used in the cell, and this occupied a little over half the volume above the frit. The gases before admission to the cell were passed through a similar vessel containing the same electrolyte, in order to saturate them with water vapor. Both the cell and the water vapor gas saturator were maintained at 80° $\pm$ 1° C. in a water bath controlled by an Electromax temperature controller. The water level in the bath was maintained by a simple float valve.[17]

Before a run, the cell and saturator were cleaned by soaking in concentrated nitric acid for about 2 hr. They were then thoroughly washed with copious amounts of distilled water. To remove the acid from the frits, large amounts of distilled water were drawn through them with a water pump. Finally, after soaking in distilled water for some time, they were washed with triply distilled water. During the washing of the cell and the saturator, the working electrodes were prepared, and the electrolyte was purified by pre-electrolysis.

The working electrodes were cleaned by heating to a white heat followed by immersion in concentrated nitric acid. After repeating this operation several times, the electrodes were washed in triply distilled water. They were then coated with platinum black by electrodeposition using a small cell, shown in Fig. 1 (b). The working electrode, F, was mounted vertically inside the center of the small glass thimble containing 2.5% chloroplatinic acid and a small concentration of lead acetate. A small, 1-cm. long platinum gauze (50 mesh) cylinder, G, which fitted closely inside the thimble was used as a counterelectrode. The platinum wire lead of the counterelectrode was sealed through the bottom of the thimble. The working electrode was platinized at a current density of 10 ma./cm.^{2} for 1 hr. During this interval it was alternately anodized and cathodized for periods of 1.5 min. by using a timer and reversal switch. The plating solution was discarded after the preparation of each electrode and was replaced by unused stock solution.

The electrolyte was pre-electrolyzed in a single compartment cell which was provided with gas inlet and outlet tubes. It held 65 cc. of electrolyte. The cell top was a 24/40 through-cone, which had two 6-mm. outside diameter tubes connected to the lower side. Platinum wire leads were sealed through these tubes. One was spot-welded to a 5-cm. long platinum gauze (50 mesh) cylinder from which a section had been removed, and the other wire was placed vertically inside the cylinder. Before use the pre-electrolysis cell and electrodes were cleaned as described above. The 5M H_3PO_4 used here was pre-electrolyzed for 60 to 100 hr. at a total current of 40 ma. using the platinum wire as the anode. The anodic current density was 62.5 ma./cm.^{2}. The electrolyte was stirred with nitrogen during the pre-electrolysis. With this arrangement, it was considered that oxidizable material would be removed at the anode, but would not be converted to the reduced state at the cathode because of the larger area and hence lower current density.

The gases were supplied to the cells through polyethylene tubes, and ground glass joint connectors were used throughout. Glass tubing was sealed to the polyethylene tubing with molten polyethylene.

The sources and grades of the materials were: hydrocarbons - Matheson, C.P. grade; nitrogen - Matheson, pre-purified grade; and phosphoric acid - Baker, analytical reagent grade.

RESULTS AND DISCUSSION

The electrodeposited platinum blacks were characterized by measurements of the lead content, crystal structure, and surface area. For the first two, the deposits were prepared on two platinum foils, 1 cm.^{2} in area, which were mounted 1 cm. apart in a cell similar to that shown in Fig. 1 (b) except that it did not contain a cylindrical platinum gauze counterelectrode. The current density (10 ma./cm.^{2}), time of plating (1 hr., during which time the electrodes were alternately anodized and cathodized as described above), temperature (25° C.), and concentration of chloroplatinic acid solution (2.5%) were identical with the conditions used in preparing electrodeposited platinum blacks on platinum wires (geometric area of 0.16 cm.^{2}) for the electrochemical measurements. The only difference between the several deposits was the amount of lead acetate contained in the chloroplatinic acid solutions. This was varied between 0 and 0.2%.

In the first two columns of Table I are shown the lead acetate concentrations and the appearances of the deposits, respectively. It will be seen that lead acetate concentrations between 0.003 and 0.05% gave black, powdery deposits, the degree of subdivision diminishing with increasing concentration, whereas lead acetate concentrations between 0.075 and 0.2% gave grey, compact deposits. The deposit prepared in the absence of lead acetate was grey and compact and was similar in appearance to those obtained with the higher lead acetate concentrations. The coulombic efficiencies, as shown in the third column of Table I, were close to 40% for all of the deposits.

The deposits prepared by Bianchi[16] using the same lead acetate concentrations were different from those described here in that they were black and very powdery, the degree of subdivision increasing with concentration. Two reasons can be presented for the differences, namely, that Bianchi used a lower concentration of chloroplatinic acid solution (1%) and a much higher current density (625 ma./cm.^{2}). A lower coulombic efficiency (≈3%) was reported. In the present work, it was shown that current densities greater than 10 ma./cm.^{2} gave rise to much gassing and a finer black deposit which tended to appear in the electrolyte as a colloidal solution. Hackerman[15] has also shown that variations in the nature of electrodeposited platinum black can result from changes in concentration and current density.

The lead content of the deposits was determined by a nondestructive X-ray fluorescence method using a standard thin film flat specimen technique.[18] A calibrated set of standards for this method was obtained by atomic absorption analysis of chemically stripped deposits. The Pb/Pt atomic ratios were calculated from the analytical data and are shown in the fourth column in Table I. In Fig. 2 is shown the plot of Pb/Pt atomic ratio vs. lead acetate concentration. It will be seen that this ratio increases almost linearly up to a lead acetate concentration of 0.08%, whereafter it tends to a constant value at higher concentrations. The deposits prepared from solutions containing 0.075, 0.1, 0.15, and 0.2% lead acetate have similar Pb/Pt atomic ratios and, as might be expected, have a similar appearance.

All the deposits gave Debye Scherrer diffraction patterns, indicating that they were crystalline. In contrast, Bianchi[16] found that the powdery deposits obtained with lead acetate concentrations from 0.08 to 0.15% gave no lines which he concluded was a result of the deposits being in a state of colloidal dispersion. An appreciable line broadening, which tends to increase with lead content, is evident in the present results, suggesting that the crystallite sizes are smaller in the higher lead containing deposits. A line shift was also observed in going from the deposit containing no lead to the one having a Pb/Pt ratio of 0.0021 and remained

constant with further increases in this ratio, in contrast to the gradual increase observed by Bianchi.[16] It would appear that the lattice constant of the lead containing deposits is greater than that of pure platinum, but it does not increase with increasing Pb/Pt atomic ratio. The diffraction patterns contained several unidentified lines which could very well be explained by a solid solution of lead in platinum, in agreement with data reported in the literature.[16]

Two methods were used to determine the areas of the platinum black electrodeposits supported on platinum wires (geometric area = 0.16 cm.^{2}). The electrodes used for this purpose were those used later in an investigation of the electrooxidation of hydrocarbons. In the first method, the area of the deposits was determined from the charge required to form a monolayer of oxygen atoms in a triangular sweep measurement.[19] In general, the electrodes were cleaned by soaking in concentrated nitric acid for 15 min., followed by washing with copious amounts of distilled water and finally with triply distilled water. They were then immersed in nitrogen stirred 5M H_3PO_4 at 80° C. contained in the cell and were held for 1 min. at 1.4v vs. NHE (Normal Hydrogen Electrode)* and then for 1 min. at 0v using an electronic potentiostat.[20] A triangular voltage sweep was then applied potentiostatically to the electrode at a sweep rate of 20 mv./sec. Typical curves, dashed and dotted lines, shown in Fig. 3, were obtained for deposits having Pb/Pt atomic ratios of 0.0021 and 0.0256, respectively. The oxidation peaks at 1.08v are the result of the formation of a monolayer of oxygen atoms on the electrode surface,[21] and the reduction peaks at 0.76v are the result of the removal of this monolayer. The area under the peaks was measured by tracing them from the photographs of the oscilloscope traces onto vellum having a uniform weight, and then weighing the appropriate cuttings. The areas under the oxidation and reduction peaks were almost identical, as would be expected. In calculating the areas of the electrodes, it was assumed that there is one oxygen atom per surface platinum atom and that there are 1.6×10^{15} sites per square centimeter.[22] The areas of the electrodes (apparent area = 0.16 cm.^{2}) are shown in the fifth column of Table I.

The second method, attempted to determine the areas of the electrodes, consisted of the measurement of double layer capacities using a single pulse technique.[23] The differential capacity was calculated from the relationship $C = i/\frac{dv}{dt}$, where i is the apparent current density and $\frac{dv}{dt}$ is the slope of the photographed trace on the oscilloscope screen. A similar procedure to that described above was used to prepare the electrodes before application of a constant current pulse. The electrode potential after the pretreatment was about 680 mv. In order to check the method and to obtain a standard of comparison, measurements were made on a bright platinum wire (geometric area = 0.16 cm.^{2}). The average of several determinations was 36 μf/cm.^{2}, and if a roughness factor of two is assumed, then the value of 18 μf/cm.^{2} obtained is in excellent agreement with those quoted in the literature.[23, 24] Although the method worked very well with the bright metal, it was less successful when applied to the finely divided metal. For one thing, because of the larger areas, and therefore larger double layer capacitances, the slopes of the potential-time traces, even for large current densities (375 ma./cm.^{2}) were very small and could not be measured very accurately. Furthermore, the traces showed a continuous curvature even after short intervals (≈10 μsec.) from the start of the pulse, thus making it extremely difficult to determine the relevant slope. However, a procedure was developed which was used for all of the deposits. With it the deposit having a Pb/Pt atomic ratio of 0.0021 was found to have a double layer capacitance of 854 μf/cm.^{2}, which is in good agreement with the value reported by Tarmy et al.[25] at the same potential. This agreement, however, may be entirely fortuitous, as the electrodeposited platinum black used by Tarmy, who did not give any details, may have been different from the one used here. Generally the areas calculated from the double layer capacities were of the same order of magnitude as those determined by the triangular sweep method, but the values were slightly lower.

*All subsequent potentials are vs. NHE unless the contrary is stated.

The lack of agreement between the two methods might be due to the difficulties encountered in applying the double layer capacity method.

In Fig. 4 is shown the plot of real area, as determined by the triangular sweep method, vs. Pb/Pt atomic ratio. It will be seen that the electrode having a Pb/Pt ratio of 0.0021 had the largest area. As the atomic ratio increases the area decreases, reaching a minimum at an atomic ratio of 0.021. The area increased slightly at higher values of the atomic ratio. The electrode containing no lead had an area between those having atomic ratios of 0.0021 and 0.021.

The activity of the several deposits toward the electro-oxidation of the hydrocarbon gases was determined using the triangular sweep method.[19] A sweep rate of 20 mv./sec. was used. The same set of electrodes was used for all of the five gases--ethane, ethylene, propane, propylene, and n-butane. However, the following procedure was used in switching from one gas to another in order to remove adsorbed species on the electrodes from the previous gas. The electrodes were held at 1.4v for 1 min. and then at 0v for 1 min. using a potentiostat before applying the triangular voltage sweep. Typical curves for propylene, full line, and dash-dot-dashed line for electrodeposits having Pb/Pt atomic ratios of 0.0021 and 0.0256, respectively, are shown in Fig. 3. The oxidation peaks at 0.75v are the result of the electro-oxidation of propylene, and the areas under these peaks in millicoulombs are used here as a measure of the electrode activity. These areas were measured by the method described previously. The areas under the oxidation and reduction peaks at 1.08 and 0.76v, respectively, were also measured.

In Fig. 5 is shown a plot of hydrocarbon oxidation (area under the oxidation peaks) vs. the Pb/Pt atomic ratio. The first thing that is evident is that ethylene and propylene are electrochemically oxidized more extensively than ethane, propane, and n-butane for all values of the atomic ratio. The curves for ethane, propane, and n-butane are identical, whereas those for ethylene and propylene differ slightly. All the gases show a maximum at an atomic ratio of 0.0021, the values for propylene and ethylene being more than four times that for the saturated hydrocarbons. At higher atomic ratios the degree of oxidation diminishes, the decline being greater for ethylene and propylene. The electrodeposit containing no lead was almost as active as that having an atomic ratio of 0.0256 in the oxidation of ethylene, ethane, propane, and n-butane. Propylene was exceptional in that the electrodeposit having an atomic ratio of 0 was almost as active as the one having a ratio of 0.0021.

Comparing Fig. 4 and 5, it is seen that the variation in degree of hydrocarbon oxidation with Pb/Pt atomic ratio closely parallels the variation of real area with this ratio. In Fig. 6 the degree of hydrocarbon oxidation vs. real area is shown. It will be seen that the degree of oxidation of the unsaturated hydrocarbons increases proportionately with real area, but that of the saturated hydrocarbons does not. In the latter case, it appears that there is some other factor limiting the oxidation as the area is increased. The data presented illustrate that area is important in the electro-oxidation of hydrocarbons and that it tends to mask any other important factors such as the effect of lattice parameter.

An important consideration in organic electro-oxidation reactions is the role of chemisorbed oxygen. On platinum, oxygen chemisorption begins at a potential of 800 mv.,[26, 27] as shown by the dashed and dotted lines in Fig. 3. The oxidation peaks of ethane, propane, and n-butane, which occur at 0.56, 0.59, and 0.56v, respectively, do not overlap the peak for "O" formation at 1.08v, but the peaks for ethylene and propylene, which occur at 0.71 and 0.77v, respectively, do. It is seen in Fig. 3 that the oxidation peak at 1.08v and the reduction peak at 0.76v in the propylene curves are, respectively, greater and smaller than the corresponding peaks in the nitrogen curves. The effect becomes smaller with increasing Pb/Pt atomic ratio. It appears that propylene is oxidized in the potential region where "O" chemisorption takes place and the latter is inhibited, since a smaller oxygen

reduction peak is observed. Ethylene behaves similarly to propylene, except that the effect described is more pronounced. Propane and n-butane are similar in that the peaks at 1.08 and 0.76v are identical with the corresponding peaks in the nitrogen curves, suggesting that oxidation of the hydrocarbons does not take place in the oxygen chemisorption region. In fact, the hydrocarbon reactions appear to be inhibited by surface oxygen.[12] Ethane behaves differently from the other four hydrocarbons in that the peaks at 1.08 and 0.76v are both greater by the same amount than the corresponding peaks observed with nitrogen. It is suggested that this is due to the reversible formation of an oxidation product of ethane in the oxygen chemisorption region.

CONCLUSIONS

1. The lead content of electrodeposited platinum black, prepared from 2.5% chloroplatinic acid at a current density of 10 ma./cm.^{2} for 1 hr. increases with lead acetate concentration. The Pb/Pt atomic ratio increases almost linearly up to a lead acetate concentration of 0.08%, whereafter it tends to a constant value with further increases of concentration.

2. The real area of the platinum black electrodeposits is a maximum at an atomic ratio of 0.0021.

3. The degree of hydrocarbon oxidation varies with Pb/Pt atomic ratio as does the real area, and the effect is much greater for ethylene and propylene than for ethane, propane, and n-butane. The electrodeposits having a Pb/Pt atomic ratio of 0.0021 have the greatest activity.

4. Other factors, such as lattice parameter, that might be important in the electro-oxidation of the hydrocarbon gases are masked completely by the area effect.

5. Ethylene and propylene continue to be oxidized in the potential region where oxygen is chemisorbed on platinum. In the process oxygen chemisorption is inhibited. The electro-oxidation of propane and n-butane is inhibited by surface oxygen.

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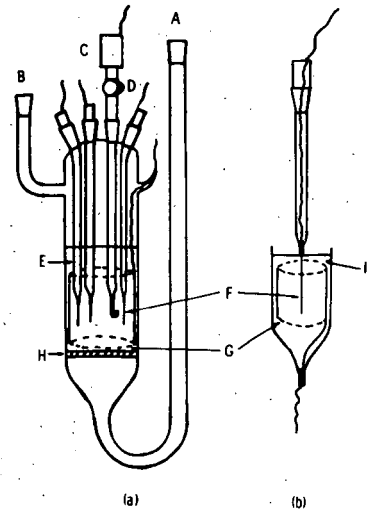
TABLE I

PROPERTIES OF PLATINUM BLACK ELECTRODEPOSITS

Lead Acetate Concentration in Plating Solution (%)	Appearance of Deposits	Coulombic Efficiency (%)	Atomic Ratio (Pb/Pt)	Real Area Per Geometric Area of 0.16 Cm.^{2} (cm.^{2})
0	Grey, compact		0	57.3
0.003	Black, very powdery	40.6	0.0021	85.4
0.01	Black, very powdery	35.9	0.0041	81.4
0.05	Black, powdery	37.2	0.0143	41.7
0.075	Grey, compact	41.6	0.0208	36.7
0.1	Grey, compact	41.6	0.0230	47.4
0.15	Grey, compact	39.8	0.0247	
0.2	Grey, compact	38.4	0.0256	47.4



A - gas inlet
B - gas outlet
C - saturated calomel reference electrode
D - closed stopcock
E - 5M H_3PO_4
F - working electrode
G - platinum gauze counter-electrode
H - coarse glass frit
I - 2.5% chloroplatinic acid solution

Fig. 1. (a) Electrochemical cell. (b) Working electrode preparation cell.

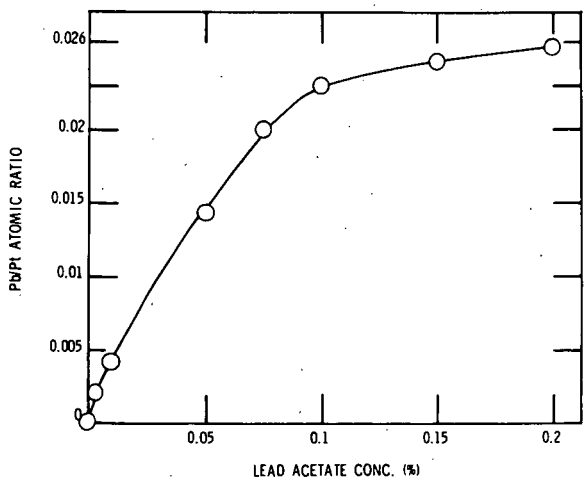


Fig. 2. Pb/Pt atomic ratio of electrodeposited platinum black prepared from 2.5% chloroplatinic acid solutions containing different lead acetate concentrations.

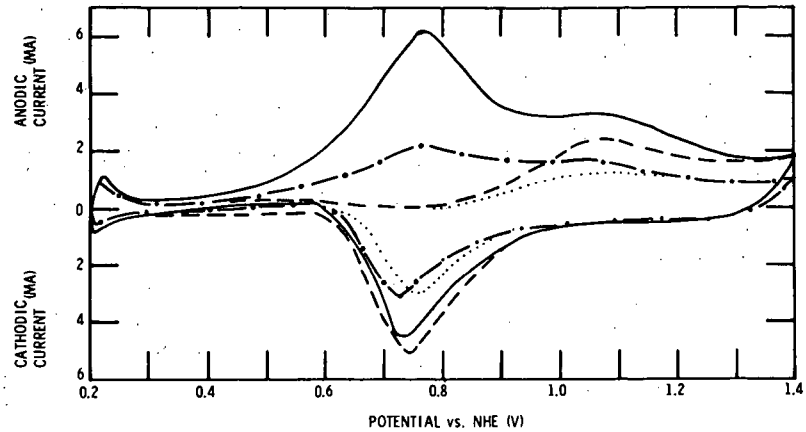


Fig. 3. Potential sweep curves on electrodeposited platinum black, in 5M H_3PO_4, at 80° C. Full line - propylene, dashed line - nitrogen, Pb/Pt = 0.0021; dash-dot-dashed line - propylene, dotted line - nitrogen, Pb/Pt = 0.0256.

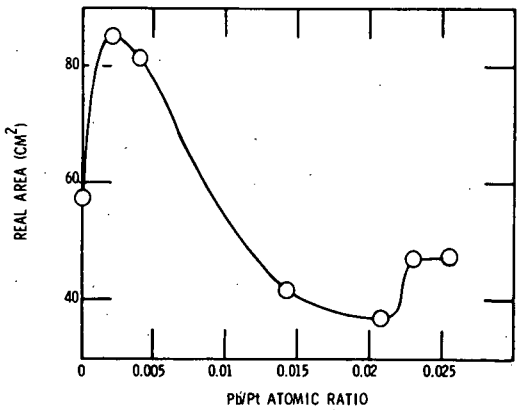


Fig. 4. Real area of electrodeposited platinum black prepared from 2.5% chloroplatinic acid solutions containing different lead acetate concentrations. Variation with Pb/Pt atomic ratio.

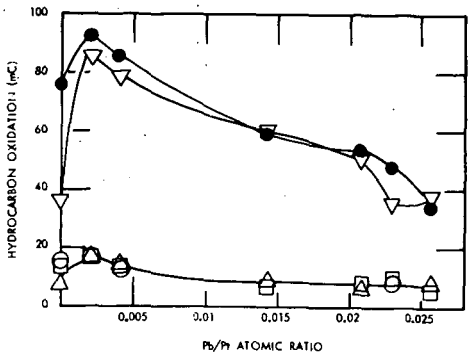


Fig. 5. Hydrocarbon oxidation (5M H_3PO_4, 80° C.) on electrodeposited platinum black prepared from 2.5% chloroplatinic acid solutions containing different lead acetate concentrations. Variation with Pb/Pt atomic ratio. □, ethane; ○, propane; △, n-butane; ▽, ethylene; ●, propylene.

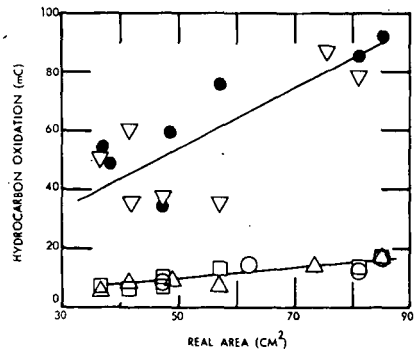


Fig. 6. Hydrocarbon oxidation (5M H_3PO_4, 80° C.) on electrodeposited platinum black prepared from 2.5% chloroplatinic acid solutions containing different lead acetate concentrations. Variation with real area. □, ethane; ○, propane; △, n-butane; ▽, ethylene; ●, propylene.