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A Discussion of Some Results in Gas Phase and Electrocatalytic Oxidation of Hydrocarbons

Before the 1960's, the oxidation of hydrocarbons on group VIII noble metal catalysts was not studied to a great extent probably because the complete oxidation to carbon dioxide and water was the only reaction found (*1, 2*). After Kemball and co-workers (*3, 4*) observed that some partial oxidations also occur, interest increased and several research groups have investigated this subject during the last 10 yr (*3–13*). In the same period, the field of electrocatalysis emerged. This term was used for the first time in 1963 (*4*). Because of the interest in fuel cells, considerable effort was devoted to the electrocatalytic oxidation of hydrocarbons. The gas phase and electrocatalytic work on hydrocarbon oxidation led to related results and conclusions but few correlations were made. It is the purpose of this communication to correlate some of the results found in these areas of investigation. Since the results are not conclusive in the gas phase as well as the electrocatalytic oxidation it can be hoped that an increased exchange of ideas between these fields will further the understanding of the processes involved.

Before discussing these subjects in some detail let us compare the gas phase and electrocatalytic oxidation of hydrocarbons in a general way. In electrocatalytic systems such as fuel cells oxygen is brought in contact with the electrocatalyst at the cathode. There adsorption and reduction of the oxygen takes place whereby water is formed in systems having acid electrolytes. The hydrocarbons are brought in contact with the electrocatalyst at the anode and are, after adsorption, oxidized by adsorbed water from the electrolyte. Thus the electron receiving and producing processes are completely separated and much of the energy released in the hydrocarbon oxidation can be gained as electrical energy. In gas phase catalysis the hydrocarbon and oxygen adsorb and react on the same catalyst surface. Often the reduction–oxidation mechanism was found to take place (*15–21*). This mechanism was established mainly with oxide catalysts but applies also to metal catalysts. According to this mechanism, the oxygen becomes adsorbed and reduced at some surface sites while the hydrocarbon adsorbs and reacts at other sites. Thus, in gas phase catalysis electron receiving and producing reaction steps are separated as well, but in a microscopic scale. Since there is a "chemical short circuit" in this case the energy is evolved as heat, but mechanistically there is considerable analogy between such a hydrocarbon oxidation process and the electrocatalytic oxidation in fuel cells.

Now let us discuss some of the results in gas phase and electrocatalytic oxidation of hydrocarbons on group VIII noble metals and gold. Kemball and co-workers (*3, 4*), Geberich, Cant and Hall (*7*) and Cant and Hall (*8–11*) studied the catalytic gas phase oxidation of olefins on such catalysts and found that in addition to the complete oxidation to carbon dioxide and water partial oxidation can occur. With ethylene the partial oxidation results in the formation of some acetic acid which is not further oxidized and poisons the catalyst. This inertness of the adsorbed acetic acid against oxidation indicated that the acetic acid is not an intermediate in the oxidation process which leads to carbon dioxide and water and thus, partial and complete oxidation are not consecutive but parallel reactions.

Very little was known about the reaction mechanism of the complete oxidation process but recently some observations were made in gas phase work (*11*) which support the idea that the formation of single carbon fragments is a very important step. For instance, while acetic acid poisons the catalyst, formic acid, a C_1 species, was found to be rapidly and completely oxidized (*11*). Recent work (*11*) in the oxidation of propylene supports this idea. On rhodium, ruthenium and gold, considerable partial oxidation to acrolein was found but with iridium mainly carbon dioxide and acetic acid were formed. Experiments with ^{14}C labeled propylene showed convincingly that on iridium cleavage of the double bond occurs. The C_1 fragments formed by breaking of the double bond are then rapidly oxidized to carbon dioxide and water while the multiple carbon fragments are more difficult to oxidize and can become stabilized by the formation of the acetic acid.

These observations and conclusions agree with a large body of information obtained in the electrocatalytic oxidation of hydrocarbons in systems with acid electrolytes. Using the multipulse potentiodynamic technique Gilman (*22, 23, 27*) Niedrach and co-workers (*24–26*) and Burshtein *et al.* (*28–30*) observed that the oxidation of hydrocarbons on platinum electrodes takes place in two different potential regions, one below and one above 0.8 V (vs the reversible hydrogen reference electrode). With ethane, propane or higher hydrocarbons a well-defined oxidation peak at potentials below 0.8 V and a more diffuse peak at higher potentials was found. With methane, a C_1 hydrocarbon, only the peak at low potentials was observed. These findings as well as the coincidence of the position of the well-defined oxidation wave in the lower potential region with the oxidation waves of C_1 species such as formic acid and "reduced CO_2" (*31*) led to the conclusion that the easily oxidized species giving rise to the wave at low potentials is a C_1 species which was termed type I (*22–25*). This type I species is believed to be partially oxidized because it was found to be not (*22*) or not as readily (*25*) desorbable by a cathodic pulse as the adsorbed species which gives rise to the wave at potentials above 0.8 V. The latter species is referred to as "type II." This type II species can be completely desorbed by a cathodic pulse which led to the conclusion that it consists of partially dehydrogenated multiple carbon hydrocarbons. Also work by Brummer and coworkers (*32–34*) indicated that a partially oxidized C_1 species, termed "O-type," plays an important role in the electrocatalytic oxidation of hydrocarbons.

The electrocatalytic oxidation of unsaturated hydrocarbon was studied extensively by Bockris and co-workers (*35–38*) by determining current potential relationships. The results obtained and conclusions made are similar to those in gas phase catalytic oxidation of unsaturated hydrocarbons (*3–13*). This will be briefly outlined in the following. In both fields a negative dependence of the rates on the olefin pressure was observed in the case of platinum catalysts or electrocatalyst respectively. Consequently it was concluded in gas phase as well as electrocatalysis that coverage by olefins on platinum is extensive and that the rate determining step on this metal involves the oxidizing species only. Thus, for the electrocatalytic olefin oxidation, the oxidative adsorption of water from the electrolyte to yield an adsorbed hydroxyl group was suggested to be rate determining (*35–38*). In the gas phase studies the adsorption of oxygen was proposed to be the rate determining step with catalysts like platinum or palladium where negative reaction orders in olefin were found (*7, 8*). The activation energies for the oxidations of various olefins were found to be in the range from 20 to 24 kcal/mole in the electrocatalytic and from 17 to 23 kcal/mole in the gas phase work (*3–13, 35–38*). The similarity of the activation energy values in these two areas is surprising considering that different oxidizing species are believed to be involved. In contrast to the results with platinum, positive dependencies of the rates on the olefin pressure were found with rhodium and iridium in gas phase as well as electrocatalytic work.

The selectivities of catalysts in olefin oxidation are quite similar in gas phase and electrocatalysis. Platinum is always very little selective, i.e., it promotes mainly the complete oxidation (*3–13, 35–38*). Palladium is quite selective in the gas phase as well as electrocatalysis (*4, 5, 7, 35–38*). With gold a somewhat higher selectivity was found in electrocatalysis than in the gas phase work. Rhodium was found in both fields to be quite unselective in the oxidation of ethylene (*9, 38*). In contrast to this, rhodium as well as ruthenium and gold showed considerable selectivity in the oxidation of propylene in gas phase work (*9, 10*). This selectivity in the case of propylene oxidation appears to be due to the formation of a symmetric allylic intermediate which is evidenced by kinetic isotope effects observed with deuterated propylenes (*9, 10*). Such intermediates are of course not possible with ethylene. No data on electrocatalytic oxidation of propylene on noble metals other than platinum were found in the open literature. The selectivity of palladium for catalytic gas phase oxidation of ethylene was found to increase with the oxygen coverage of the catalyst (*7*). In connection with this observation it is interesting that in the electrocatalytic oxidation of ethylene on palladium a higher selectivity, i.e., more of the partial oxidation products, was found when the experiments were carried out at 0.8 V than at 0.6 V (*38*). Since at 0.8 V palladium is more oxidized than at 0.6 V it seems possible that the different selectivities are also in the electrocatalytic oxidation due to the oxygen coverages.

The similarities between gas phase and electrocatalytic hydrocarbon oxidation outlined above are remarkable considering that different oxidizing species are believed to be involved in these two areas. Also the state of the catalyst surfaces is different. In the gas phase catalytic oxidation there is considerable coverage of the noble metal catalysts by oxygen and the chemisorbed oxygen is generally believed to be the oxidizing species. In the electrocatalytic oxidation the surfaces of the noble metal electrocatalysts are not covered by oxygen at the potentials where most of the hydrocarbon oxidation occurs and adsorbed water is the oxidizing species. Water is known to play a role as oxidizing species not only in the electrocatalytic oxidation but also in certain biochemical oxidation reactions. However, it has not been considered in the past as an oxidizing species in gas phase heterogeneous catalytic oxidation. Therefore it is interesting that recently two research teams (*39–42*) found strong indications that water is involved in the heterogeneous catalytic oxidation of hydrocarbons on palladium and platinum. Seiyama *et al.* (*39–40*) showed that the rate of the vapor phase oxidation of mixtures of propane, oxygen, water and nitrogen at 100°C is strongly dependent on the partial pressure of water. These authors recognized also that water plays a role in the oxidation of olefins on palladium and platinum catalysts suspended in aqueous solutions. Platinum catalyzed mainly the complete oxidation while with palladium partial oxidation also was found. Moro-oka *et al.* (*41–42*) investigated the oxidation of propylene on palladium using mixtures of propylene, oxygen and ^{18}O labeled water. They found that the oxidation of the olefin on a palladium catalyst took place according to the following reaction scheme in which A stands for olefin: $A + 1/2\ O_2 + H_2O^* \rightarrow AO^* + H_2O$. These authors demonstrated that exchange reactions are not responsible for the fact that the oxygen from the water appeared on the olefin. Therefore it was concluded that the water oxidized the olefin and gas phase oxygen was reduced to water. Thus, a mechanism of heterogeneous catalytic gas phase oxidation was found which corresponds to the mechanism of electrocatalytic hydrocarbon oxidation in which, as discussed before, the hydrocarbons are oxidized on the anode by adsorbed water and the oxygen is reduced on the cathode whereby water is formed. Confirmation of these findings of Seiyama *et al.* and Moro-oka *et al.* by other investigators would be desirable.

In hydrocarbon oxidation without intentionally added water a related mechanism can be visualized. On catalysts such as platinum and palladium dissociative adsorption of alkanes has been widely observed. Infrared spectroscopy work shows that at the temperatures under consideration extensive dissociative adsorption of olefins can be expected also (*43*, *44*). The adsorbed hydrogen atoms formed by dissociative adsorption of the hydrocarbons will react with adsorbed oxygen at considerably higher rates than with the adsorbed hydrocarbons. This can be concluded from the low temperatures at which hydrogen oxidation occurs on the surfaces of platinum metals (*45*) as well as from the fact that selfhydrogenations such as observed under nonoxidizing conditions do not occur during oxidation reactions (*8*). The reaction between the adsorbed hydrogen atoms and adsorbed oxygen will result in surface hydroxyl groups which may play a role in the oxidation of hydrocarbons as is the case in the electrocatalytic oxidation.

The results discussed in this communication lead to the conclusion that the reaction mechanisms of gas phase and electrocatalytic oxidation of hydrocarbons may be more closely related than assumed in the past. Before closing it seems pertinent to discuss the question of dissociative adsorption of water. In electrocatalysis, the oxidizing species is formed on the anode by adsorption of water ($H_2O \rightarrow OH + H^+ + e$). This reaction is thermodynamically more favorable than the dissociative adsorption of water from the gas phase because the solvation energy of the proton is high. Dissociative adsorption of water from the gas phase was observed on tungsten (*46*). With platinum the results are not conclusive. Changes of the surface potential of atomically clean (110) oriented platinum films upon exposure to water are believed to be due to dissociative adsorption of water leading to a coverage by hydroxyl groups and hydrogen evolution (*47*). Eley *et al.* (*48*) used the concept of dissociative adsorption of water on platinum in the interpretation of some infrared results (*48*). However Darensbourg and Eischens (*49*) investigated this problem in more detail using both H_2O and D_2O. Very similar bands were obtained with H_2O and D_2O which indicated that the infrared bands were not due to dissociative chemisorption of water. They could be attributed to impurity carbon monoxide.

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