

OXIDATION AND ADSORPTION OF HYDROCARBON ON NOBLE METAL ELECTRODES. 6. A discussion of the Mechanism of Saturated Hydrocarbon Oxidation on Pt.

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ABSTRACT

The mechanism of the anodic oxidation of saturated hydrocarbons on Pt electrodes in strongly acid solutions at elevated temperatures is discussed. Since the coulombic efficiency for  $\text{CO}_2$  production is 100% even for complex fuel molecules, the need to examine the adsorption processes in order to obtain mechanistic information is emphasized. From adsorption studies it has been found that three principal types of material accumulate in the steady state adsorbate: these are  $\text{CH}-\beta$  (polymeric),  $\text{CH}-\alpha$  (mixture of alkyl radicals), and O-type (oxygenated  $\text{C}_1$  species). The O-type is the predominant species and oxidizes the most readily at high potentials. Its coverage is high below about 0.4 v. This coverage is insensitive to hydrocarbon pressure. This observation, coupled with previous reports that the overall reaction order is unity, prompts the suggestion that O-type is a poison for the overall hydrocarbon-to- $\text{CO}_2$  reaction. However, recent results indicate that in the region of high coverage the overall reaction order is considerably less than unity and even negative at low potentials. This suggests that the slow step of the overall reaction involves a reaction of an adsorbed species (e.g. O-type) at high or limiting coverage. A tentative overall mechanism for the oxidation of hydrocarbons is suggested.

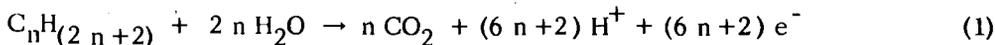
INTRODUCTION

The anodic oxidation of saturated hydrocarbons is required for the economic utilization of the fuel cell principle. Consequently, there has been much interest in this area in the past five years. The earliest reports of saturated hydrocarbon oxidation at low temperatures and interesting rates were by Grubb and Niedrach (1) in 1963. They used extensive amounts of Pt as the anode catalyst and concentrated  $\text{H}_3\text{PO}_4$  at  $150^\circ\text{C}$  as the electrolyte and achieved moderate current densities at reasonable potentials. Since then there has been a large number of studies and it is clear that while many saturated hydrocarbons can be oxidized the kinetics are rather unfavorable. The ultimate utilization of the hydrocarbon anode requires an enhancement of these kinetics, or requires the development of a sufficiently cheap, i.e. non-noble metal, catalyst that the electrode area can be appropriately expanded.

It appears that maximum activity is found for the  $\text{C}_2 - \text{C}_4$  (2,3) range that straight chain hydrocarbons are better than bridged chains (4) and that Pt is one of the better catalysts that we have (5). In the present work, we have undertaken to investigate the mechanism of anodic hydrocarbon oxidation with a view to elucidating those features, structural, electronic and ionic, which determine the path and the rate of the overall reaction. In the first instance we have studied the adsorption and oxidation of  $\text{C}_3\text{H}_8$  (6,7,8) and  $n\text{-C}_6\text{H}_{14}$  (9) at elevated temperatures using hot concentrated  $\text{H}_3\text{PO}_4$  and smooth Pt electrodes. While the chemical mechanism has not been fully unravelled at this point, a number of significant features of the reaction path have been revealed and the present paper summarizes the result of our own work and discusses mechanistic conclusions which can be drawn, both from our own work and from that of others.

## OVERALL COURSE OF REACTION

It is well known that saturated hydrocarbons are very stable materials and it would be expected that their oxidation would be very difficult, and indeed as mentioned, stringent conditions are required for the reaction to occur at any reasonable rate. By analogy with gas phase reactions and in particular, the heterogeneous catalysis reactions of these compounds, one might expect that the reaction path would be very complicated and as a consequence that there would be a number of products. However, it has been shown that the general reaction



occurs to completion with no side products accumulating in the solution or in the gas phase (10, 3, 11).

This 100% faradaic efficiency for the product of  $CO_2$  is remarkable and unexpected and has important mechanistic implications. Thus following the initial adsorption all the intermediate products between the reactant and the final product,  $CO_2$ , are adsorbed on the electrode. There is no other way to account for the observations. This suggests that the fruitful way to investigate the reaction mechanism is to study the adsorption processes. This has been the prime approach of our experiments and in conjunction with the work of others, notably Gilman (12) and Niedrach (13-17), it has led to a considerable understanding of the nature of the products formed on the electrode.

## NATURE OF ADSORBED PRODUCTS

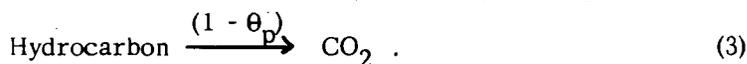
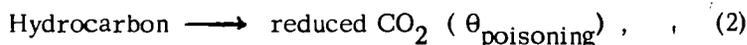
The methods we have used to examine the adsorbed products involve their determination with anodic stripping and with H-atom deposition. Using these techniques in conjunction with controlled potential adsorption regimes onto a clean electrode, we can define the charge to oxidize the adsorbed species,  $Q_{ads}$  and their coverage  $\theta_{org}$ . From the relationship between  $Q$  and  $\theta_{org}$  we can determine  $[e]$  which is the number of electrons released when the adsorbed product is oxidized to  $CO_2$ . This is quantitatively of prime importance in discussing the nature of the adsorbed products and their likely relationship to the overall reaction.

We have shown that when  $C_3H_8$  (8) or  $n-C_6H_{14}$  (9) are adsorbed, three partially oxidized residues accumulate on the electrode. These residues are of three generic types: the CH- $\alpha$ , the CH- $\beta$  and the O-type. The CH- $\alpha$  is cathodically desorbable, relatively unreactive towards oxidation and probably comprises a mixture of (partly dehydrogenated) alkyl radicals. Its composition changes with potential. The composition of the CH- $\beta$  species is also a function of potential. It is unreactive towards both reduction and oxidation and is probably a carbonaceous polymer. The O-type, the major species in terms of coverage, has the same composition at all potentials. It releases  $\sim 1.3$  electrons per covered site on oxidation to  $CO_2$  and this indicates that it is oxygenated. We have found (18) that O-type is electrochemically identical to the reduced  $CO_2$  species of Giner (19), confirming his results (20).

Other workers have also reported evidence for these types of adsorbed product. Niedrach et al (14) following Gilman's (12) suggestion have suggested two distinct paths which the initially adsorbed hydrocarbon can adopt. The first path, the preferred path, involves the production of what we would call O-type. The second path involves the production of what we would call CH- $\alpha$ . The distinction between the types was based on the current waves which appeared during the

linear anodic sweep stripping of the adsorbed layer. The fact that O-type was oxidized more readily under these conditions than CH- $\alpha$  was taken to mean that those reactions leading to O-type were preferable to those leading to CH- $\alpha$ . In support of this view we may note that CH- $\alpha$  plays a greater rôle with higher hydrocarbons which are less reactive. The implication of this view of course is that the production of O-type and CH- $\alpha$  are parallel reactions.

We found that (8,9) oxidation kinetics of O-type are faster than those of CH- $\alpha$  and that its coverage is high compared with CH- $\alpha$ . These observations support the view of Niedrach. However, there is a large difficulty. The corollary of this view would be that at low potentials the oxidation of O-type is the rate limiting step in the overall reaction with a very slow side reaction involving CH- $\alpha$  oxidation in parallel with it. If this were so, we would expect that variations in the rate of O-type oxidation with potential and with hydrocarbon concentration would closely parallel the variation of the rate of the overall reaction. Since it has been reported that the overall reaction for both C<sub>3</sub>H<sub>8</sub> (11) and n-C<sub>6</sub>H<sub>14</sub> (21) is first order with respect to fuel pressure, we would expect  $\theta_{\text{O-type}}$  to be strongly pressure dependent. However, we found O-type coverage for both C<sub>3</sub>H<sub>8</sub> and n-C<sub>6</sub>H<sub>14</sub> to be almost independent of fuel pressure (8,9). This led us to the view that the reaction occurs via a general mechanism which was recently proposed (22), i.e.



In this mechanism the overall reaction occurs on that part of the electrode which is not occupied by adsorbed species, or at least is not occupied by the poisoning adsorbed species. It was suggested that reduced CO<sub>2</sub>, i.e. O-type, was the worst kind of poisoning species since being a C<sub>1</sub> species it very likely consumed just those C<sub>1</sub> reactive radicals which maintain the rate of the overall reaction. This view is in sharp contrast to that of Niedrach et al and suggests that those reactions which lead to the production of O-type are undesirable.

Since some adsorbed species must be controlling the rate of the overall reaction, we suggested the possibility that the CH- $\alpha$  species comprises several parts (8,9). Some of these parts, following Niedrach et al (14) are undesirable but some of them, the CH- $\alpha_{\text{active}}$ , were desired to promote the overall reaction.

### REACTION ORDER

As indicated, a central point in the divergence of our view from that proposed by Niedrach et al is the reaction order. In an early study we reported that the reaction order on smooth Pt is positive (23). Recently it has been reported (11, 21) that on platinized Pt the reaction order for C<sub>3</sub>H<sub>8</sub> and n-C<sub>6</sub>H<sub>14</sub> is accurately unity. These experiments, on platinized Pt, were the reasons for our adopting the views expressed above.

We have, however, reexamined the reaction using platinized Pt and two important points have emerged.

Firstly, we have found that coverage with O-type, is much more dependent on fuel concentration than it is on smooth Pt. For example, at 0.35 v on smooth Pt at 130°C the O-type concentration does not change when the C<sub>3</sub>H<sub>8</sub> pressure in-

creases from 2.2 mm to 223 mm (8). Similar insensitivity is found with n-C<sub>6</sub>H<sub>14</sub> (9). On platinized Pt, however, the concentration of O-type increases by from 0 to ~ 250  $\mu\text{coul/r.cm}^2$  for C<sub>3</sub>H<sub>8</sub> under the same conditions (24). These observations prompted us to examine the order of the reaction.

This second and crucial finding was that at low potentials, e. g. below 0.35 v, the reaction order is not unity. In fact, we find a small negative order for the overall reaction rate (24) and this is precisely the kind of complication which would be expected if the reaction were coming under extensive adsorption control at relative high coverage. There is little experimental conflict between our results and those reported by Gilcadi et al (11) since most of their studies refer to the potential region above 0.35 v where the coverage with adsorbed materials becomes very low.

#### RELATION OF ADSORBED PRODUCTS TO OVERALL REACTION

These observations show that there is still a sharp disagreement between the orders of the overall reaction and of O-type coverage. However the results are more ambiguous than was previously thought (8). The unity order for the overall reaction reported by Gilcadi, Stoner and Bockris for C<sub>3</sub>H<sub>8</sub> oxidation (11) implies a relatively simple mechanism. Specifically, the reaction could not proceed via O-type since the coverage with O-type was thought to be high and virtually independent of C<sub>3</sub>H<sub>8</sub>-pressure (8). For this reason, we postulated that the reaction proceeded on the part of the surface not occupied by O-type, a similar poisoning mechanism to HCOOH oxidation (22, 25). The negative reaction order we have observed in conjunction with the increase in O-type coverage with pressure on platinized Pt (24), could certainly be interpreted in terms of such a poisoning mechanism (reactions (2) and (3)). However, these results on the overall order show that at low potentials the reaction could proceed via an adsorbed species present at high coverage, e. g. O-type.

Consideration of such a mechanism allows an alternative interpretation of the data. Thus we note that coverage with CH- $\alpha$  has an even stronger dependence on C<sub>3</sub>H<sub>8</sub> pressure than has O-type for smooth (8) and for platinized Pt (24). If the oxidation of O-type involved a "reactant pair" mechanism, involving the adsorbate itself and free sites, as postulated by Gilman for CO<sub>ads</sub> (26), CH- $\alpha$  could act as a poison for the reaction due to its occupation of surface. Since CH- $\alpha$  is so pressure dependent, we can entertain this mechanism as an explanation of the above conflict in reaction order whilst still asserting that the main reaction proceeds via O-type. We have found an increase in the rate of O-type oxidation in circumstances where we deliberately desorb CH- $\alpha$  (24) and this supports such a mechanism.

These observations allow possibly the maintenance of the views expressed by Niedrach et al concerning the role of O-type. A third observation with platinized Pt electrodes leads to further elaboration of the mechanism. We have investigated the oxidation kinetics of the adsorbed species on platinized Pt in presence of C<sub>3</sub>H<sub>8</sub> with anodic chronopotentiograms. These were taken at sufficiently low current densities that the adsorbate oxidation occurs well before the electrode's oxidation but at sufficiently high current densities that insignificant solution C<sub>3</sub>H<sub>8</sub> is oxidized. Two predominant features are observed, a prewave and a more extensive potential plateau (24). The behavior of the plateau leaves no doubt that it corresponds to the oxidation of O-type material, i. e. reduced CO<sub>2</sub>. The oxidation rate corresponding to the plateau is about 40-50% of the overall reaction rate of the hydrocarbon. This is a reasonable value if O-type lies between C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> and indeed strongly suggests this conclusion.

The prewave is associated with adsorbed material on the electrode other than O-type, presumably CH- $\alpha$ . At low currents, the prewave is found at lower potentials than O-type but at high oxidation rates it merges into the O-type wave. Eventually, both processes are displaced to the region of electrode oxidation. The crucial point is that whereas at high potentials (e. g. in our "anodic desorption" experiments (8, 9) or in fast linear sweeps (12, 14)) CH- $\alpha$  will oxidize less easily than O-type, it oxidizes more readily at low potentials. The relative oxidation rates at low potentials are what are significant for the operation of the hydrocarbon anode. Hence we can no longer assert that formation of CH- $\alpha$  is necessarily undesirable. Similarly, our previous conclusion (8, 9) that CH- $\alpha$  production is parallel to O-type production can no longer be maintained.

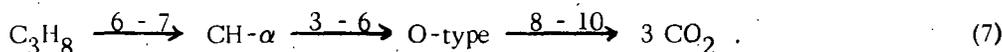
There is no reason to suppose that the reaction sequence



does not occur.

If this is so, the oxidation of O-type must be rate-limiting at least as far up the homologous series as n-C<sub>6</sub>H<sub>14</sub>. This is because O-type's coverage is so high. An additional complication may also arise from the above-mentioned poisoning of O-type oxidation by CH- $\alpha$  occupying the surface. As the homologous series is ascended, CH- $\alpha$  coverage increases and at some stage it is clear that its reaction, reaction (5), becomes rate limiting.

From the coulometry of the adsorbed species, we have suggested the following numbers of electrons in these various reactions (24):



Confirmation of this reaction mechanism is required and, in particular, the chemical structures of the intermediates are the aim of our further work.

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