

THE ADSORPTION AND OXIDATION OF HYDROCARBONS ON NOBLE METAL ELECTRODES  
Part II.-PROPANE ADSORPTION ON SMOOTH Pt AT ELEVATED TEMPERATURES

by

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I. INTRODUCTION

The over-all aim of the present series of papers is to provide the basic scientific understanding of the functioning of a noble metal hydrocarbon anode. To this end, a study has been reported of the chemisorption of  $C_3H_8$  from 13M  $H_3PO_4$  solutions onto smooth Pt electrodes<sup>1</sup>. In that work, measurements were reported for experiments made mainly at 80°C but some data were also taken at 110°C. In the present work, the previous experiments have been extended to 140°C, which is close to the region of effective operation of a hydrocarbon fuel cell<sup>2</sup>. As will be seen, most of the conclusions of the previous work can be carried over to the higher temperature region although some modification of the views on the structure of the residues which are adsorbed is obtained from the experiments presented here.

II. EXPERIMENTAL

Most of the experimental procedures have been described previously<sup>1,3,4,5</sup> and only the essential parts will be described here.

Experiments were carried out at 110°, 130°, and 140° ( $\pm 0.5^\circ$ ) using electrolyte solutions of 13M  $H_3PO_4$  purified with  $H_2O_2$ <sup>1</sup> saturated with  $N_2$  or  $C_3H_8$ , as required. The electrodes were Pt wires sealed in soft glass or, in experiments where very good approximation of semi-infinite linear diffusion was required, they were small flat flags. The electrodes were heated in an oxidizing gas flame, before use, to minimize surface roughening in the concentrated acid<sup>1</sup>. Potentials were measured against the autogeneous  $H_2$  reference electrode described by Giner<sup>6</sup> and converted to the reversible hydrogen electrode in 13M  $H_3PO_4$  at each temperature (R.H.E.).

Unless otherwise stated (cf. Glossary of Symbols), our results are expressed in terms of "real  $cm^2$ ". A real  $cm^2$  is defined in terms of the maximum cathodic galvanostatic charge for depositing H atoms on a clean electrode prior to  $H_2$  evolution. It is assumed that this quantity, after correction for double layer effects, is 210  $\mu$  coulomb/ $cm^2$  (see reference (4) for a discussion of this point). This value of 210  $\mu$  coulomb/ $cm^2$  is taken as the reference value of  $Q_d^t$  at each temperature (cf. ref. (1)). A "clean electrode" is defined as one which has recently been anodized according to the procedure described below.

The basic experimental technique used in this study, as before<sup>1</sup>, involves the rapid sequential manipulation of the electrode's potential so as to bring its surface, and the solution in its vicinity, into a reproducible and well-defined condition. This method has been used extensively by Gilman<sup>7</sup> and the major departure from his procedure is the use of a galvanostatic pulse rather than a linear potential sweep to sample the surface. Prior to each measurement the electrode potential was raised to 1.35v. This allows the oxidation and desorption of adsorbed impurities and results in the formation of a passive oxide layer. During the first part of this treatment (1/2 min.), the solution in the vicinity of the electrode is vigorously gas-stirred to sweep away any desorbed impurities. Then the solution is allowed to become quiescent to establish the bulk concentration of  $C_3H_8$  at the electrode (its reaction rate at 1.35v is very low). The oxide is reduced at 0.1v for 10 - 100 msec. and, since no  $C_3H_8$  is adsorbed at 0.1v (see later), this brings the electrode into a clean and reproducible surface condition. The electrode is then brought to the potential of interest, E, for a time  $\tau_E$ . Then an anodic or cathodic galvanostatic pulse is applied to sample the surface. This potential sequence is shown in Fig. 1.

To assist the presentation and discussion of the data, the symbols used in this paper are summarized in Table I.

### III. RESULTS AND DISCUSSION

#### Anodic Charging Curves

In situ anodic stripping is one of the most direct and obvious methods of attempting to measure adsorption on a solid electrode and it has been used widely in the study of adsorption of organic substances on Pt (see, for example, references (3)-(5) and (7)-(12)). A considerable problem for smooth Pt electrodes is that at anodization rates which are fast enough to prevent significant re-adsorption during the pulse the oxidation of the adsorbate is usually pushed into the region of electrode oxidation. This complicates the interpretation of the charges obtained with anodic pulse methods. In addition to a charge,  $Q_{\text{electrode}}$ , due to oxidation of the electrode, some charge,  $Q_{dl}$ , also flows into the double layer. Charge may also be consumed in oxidizing material which diffuses up to the electrode during the pulse,  $Q_{\text{diff}}^{\text{C}_3\text{H}_8}$ . The total anodic charge under  $\text{C}_3\text{H}_8$  in the potential region prior to  $\text{O}_2$ -evolution

(cf. Fig. 2),  $(Q_{\text{anodic}}^{\text{total}})^{\text{C}_3\text{H}_8}$ , is then

$$(Q_{\text{anodic}}^{\text{total}})^{\text{C}_3\text{H}_8} = Q_{\text{ads}}^{\text{C}_3\text{H}_8} + Q_{\text{electrode}} + Q_{\text{diff}}^{\text{C}_3\text{H}_8} + Q_{dl} \quad (1)$$

The quantity of interest is the charge passed in oxidizing previously adsorbed  $\text{C}_3\text{H}_8$ ,  $Q_{\text{ads}}^{\text{C}_3\text{H}_8}$ , and it is clear that to determine it we must measure or eliminate the other quantities in equation (1).

$Q_{\text{diff}}^{\text{C}_3\text{H}_8}$  is small or negligible since we find that if  $\tau_{\text{ads}}$  is short, viz.  $< 5$  msec, so that an insignificant amount of  $\text{C}_3\text{H}_8$  is adsorbed,  $(Q_{\text{anodic}}^{\text{total}})^{\text{C}_3\text{H}_8}$  is the same as  $(Q_{\text{anodic}}^{\text{total}})^{\text{N}_2}$ . Evidently, even at elevated temperatures which are close to those obtained in a hydrocarbon fuel cell<sup>2</sup>,  $\text{C}_3\text{H}_8$  must be adsorbed before it can be oxidized and, as will be seen, there is no adsorption in the potential region of the anodic pulses (cf. Figs. 2 and 8).

Since  $Q_{dl}$  is likely to be relatively minor the major problem is the elimination of  $Q_{\text{electrode}}$ . In order to investigate a method of doing this,  $\text{C}_3\text{H}_8$  was adsorbed for 10 sec. at 0.3 v at  $130^\circ\text{C}$  and  $(Q_{\text{anodic}}^{\text{total}})^{\text{C}_3\text{H}_8}$  was measured as a function of the current density,  $i_a$ . This variation, is shown in Fig. 3 together with corresponding measurements made at 10 msec at 0.3 v under  $\text{N}_2$ . It is seen that although both quantities depend strongly on  $i_a$ , their difference is independent of  $i_a$  over more than two orders of magnitude. The simplest way to account for this behavior is to assume that  $Q_{\text{electrode}} + Q_{dl}$  are the same in  $\text{N}_2$  and  $\text{C}_3\text{H}_8$ . Then, as before (1),

$$(Q_{\text{anodic}}^{\text{total}})_{\text{C}_3\text{H}_8} - (Q_{\text{anodic}}^{\text{total}})_{\text{N}_2} = Q_{\text{ads}}^{\text{C}_3\text{H}_8} \quad (2)$$

The independence of the above difference on  $i_a$  could also be explained by assuming that  $(Q_{\text{electrode}} + Q_{\text{dl}})$  varies with  $i_a$  but that previously adsorbed propane is desorbed during the measurement also as a function of  $i_a$ . These two effects would then have to be assumed to cancel when  $i_a$  is varied. This is most unlikely as the kinetics of these processes should vary rather differently with temperature and the non-dependence of  $Q_{\text{ads}}^{\text{C}_3\text{H}_8}$  on  $i_a$  is known to occur at least from 80° to 130°. It seems clear then that the anodic charging method does give an accurate measure of the amount of oxidizable, adsorbed material. Subsequent measurements were made in the range of currents from 100-200 mA/cm<sup>2</sup> as was convenient.

#### Adsorption Kinetics at 130°C from Anodic Charging Curves

The variation of  $Q_{\text{ads}}^{\text{C}_3\text{H}_8}$  with time of adsorption at various potentials is shown in Fig. 4. The data were obtained by extrapolating the  $(Q_{\text{anodic}}^{\text{total}})_{\text{C}_3\text{H}_8}$  data to  $\tau_{\text{ads}} = 0$  at each potential and subtracting the extrapolant from each of the values. This is more accurate than the above procedure of subtracting the 10 msec  $Q_{\text{ads}}^{\text{C}_3\text{H}_8}$  values. We see that  $Q_{\text{ads}}^{\text{C}_3\text{H}_8}$  increases with  $\tau_{\text{ads}}^{1/2}$  independently of potential and, as at 80°C (1), this suggests that the initial adsorption onto a clean electrode is limited by diffusion in solution.

Assuming semi-infinite linear diffusion, with no retarding effect on the adsorption due to blockage by adsorbed material, the accumulation of material on the electrode is given by<sup>13</sup>

$$Q_{\text{ads}}^{\text{C}_3\text{H}_8} = 2n F \left[ \frac{D_{\text{C}_3\text{H}_8}^{130^\circ}}{\pi} \right]^{1/2} C_{\text{C}_3\text{H}_8}^{130^\circ} \tau_{\text{ads}}^{1/2} \text{ coulomb/geom cm}^2. \quad (3)$$

The over-all reaction of  $\text{C}_3\text{H}_8$  to  $\text{CO}_2$  has been shown to be<sup>14</sup>



and  $n$  should therefore be 20. There is convincing evidence, both from earlier results<sup>1</sup> and from those given below, that  $n$  is 17 rather than 20. This assumes that the initially adsorbed material is propane which has lost about three H atoms upon adsorption and which is oxidized to  $\text{CO}_2$  at high positive potentials. This argument also assumes that there is no turnover of adsorbed

molecules, i.e. no desorption. Then taking  $C_{\text{C}_3\text{H}_8}^{130^\circ}$  as  $6.8 \times 10^{-8}$  moles/cm<sup>3</sup><sup>15</sup>, and since the measured electrode roughness

was 2.0, we may use the initial slopes of Fig. 4 to calculate  $D_{C_3H_8}^{130^\circ}$  as  $5.0 \times 10^{-6}$  cm<sup>2</sup>/sec. The value previously found at 80°C was  $1.47 \times 10^{-6}$  cm<sup>2</sup>/sec. Using Walden's rule, these predict  $11.8 \times 10^{-6}$  cm<sup>2</sup>/sec. and  $9.3 \times 10^{-6}$  cm<sup>2</sup>/sec for  $D_{C_3H_8}^{25^\circ}$  in H<sub>2</sub>O, respectively. These are reasonable values for  $D_{C_3H_8}^{25^\circ}$  and in reasonable agreement with one another and they substantiate the conclusion that diffusion limits the initial adsorption on clean Pt.

As before, the rate of accumulation of adsorbed material on the electrode soon departs from diffusional limitation (Fig. 4). This occurs after about 6 sec, 2 sec and 0.4 sec at 0.22, 0.3 and 0.4 v respectively and takes place faster than at 80°C where the effect at corresponding potentials is significant after ~ 20-30 sec, ~ 10 sec and ~ 3 sec respectively.

As can be seen from Fig. 4, the concentration of oxidizable material becomes constant within 2 min. The values of  $Q_{ads}^{C_3H_8}$  in Fig. 8 were thus taken after 2 min. of adsorption.

#### Adsorption Kinetics at 130° from Cathodic Charging

The purpose of cathodic charging curves is to examine the electrode surface for the presence of irreversibly adsorbed residues. Since most of the present studies of C<sub>3</sub>H<sub>8</sub> adsorption were carried out at potentials in or close to the region of H-atom adsorption an additional potential step (1 - 10 msec at 0.5 v) was interpolated in the potential-time sequence just before measuring a charging curve. The purpose of this step was to displace any H-atoms, which might have been on the electrode at the lower potentials, prior to depositing H-atoms on the bare part of the electrode with the cathodic pulse. The duration of this step

was shown not to alter  $\theta_H^t$  or  $Q_{ads}^{C_3H_8}$ . The variation of  $\theta_H^{130^\circ}$  with time of adsorption and with potential is shown in Fig. 5.

At 130°C, and at 0.3 v and 0.4 v,  $\theta_H^t$  decreases with  $\tau_{ads}^{1/2}$  at essentially the same rate at each potential. This indicates, as did the anodic measurements, that adsorption is initially limited by diffusion in solution. Data at 0.2 v also follow a  $\tau^{-1/2}$  relation but with a different slope. C<sub>3</sub>H<sub>8</sub> is a sufficiently complex molecule that its mode of adsorption cannot be assigned a priori. Thus, each molecule of the adsorbed material could occupy one, two, three, or more Pt atoms on the surface. In order to discuss these possibilities, we calculate the diffusion-limited, adsorption rates for each mode of attachment.

The observed rate of accumulation of  $C_3H_8$  is  $1.42 \times 10^{-4}$  coul/cm<sup>2</sup>/sec<sup>1/2</sup>. If we take  $n$  as 17, this is equivalent to  $5.2 \times 10^{13}$  molecules/cm<sup>2</sup>/sec<sup>1/2</sup>. Since 1 cm<sup>2</sup> is equivalent to  $1.7 \times 10^{15}$  atoms Pt, this corresponds

to  $0.040 S \theta_H^{130^\circ}$ /sec<sup>1/2</sup>, where  $S$  is the number of Pt surface atoms occupied by each adsorbed  $C_3H_8$  molecule. (Strictly, this should be  $0.040 S \frac{17}{20-S}$  since  $n$  is a slight function of  $S$ , cf. equation (5).)

The data at 0.3v and 0.4v are well fitted by this equation for  $S = 3$ . At 0.2 v, the data follow the equation for 1 site adsorption. It seems then that the previous conclusions regarding the mode of adsorption as a function of potential are valid at 130°C. The

linearity of the  $\theta_H^{130^\circ}$  vs.  $\tau_{ads}^{1/2}$  plots over wide ranges of  $\theta$  with no apparent effect from surface blocking, i.e. the absence of a  $(1-\theta)$  term, is explained in terms of a long lived mobile adsorption-precursor state<sup>1</sup>. The main adsorption process appears to be chemisorption but the precursor may involve a small quantity of physically adsorbed material.

Departure from linearity of the  $\theta_H^t$  vs.  $\tau_{ads}^{1/2}$  plots occurs after much longer times of adsorption than do the equivalent departures of the anodic charging data. Thus, at 0.4 v, 0.3 v, and 0.2 v, respectively, significant deviations occur at  $\sim 10$  sec,  $\sim 30$  sec, and (probably) 100 sec as against  $\sim 0.4$ , 2, and 6 sec for the anodic data. As long as the adsorption follows the lines in Fig. 5, the rate of adsorption of  $C_3H_8$  molecules is essentially equal to their rate of arrival at the surface, and the distribution of the adsorbed molecules is as described above. However, when deviations from the linearity of the cathodic data are found, the surface is becoming covered with the equilibrium, or at least steady state, concentration of  $C_3H_8$  or related species at the particular potential of measurement. That this occurs later than the time required to reach saturation as judged by the  $Q_{ads}^{C_3H_8}$  vs.  $\tau_{ads}^{1/2}$  curves clearly indicates that the anodic and cathodic methods do not measure the same property of the adsorbate. This was noted previously and is also discussed below.

#### Experiments with $Cl^-$ to Investigate Variation in Mode of Adsorption with Potential

As noted above, there is a dramatic change in the mode of attachment of  $C_3H_8$  to a Pt electrode as the potential is raised from 0.2 v to 0.3 v. Thus, at all temperatures, each  $C_3H_8$  molecule adsorbed at 0.2 v occupies one Pt surface atom and, at higher potentials, more than one. At 80°C and at 0.25 v, the adsorbate which is initially attached to one site per molecule, appears to change over to the 3-site species<sup>1</sup>.

In order to account for the persistence of the singly-bonded species at 0.2 v, it is tempting to consider that the initial adsorption occurs via a primary carbon atom of the  $C_3H_8$  since this would be relatively unlikely to yield a 3-site adsorbate. Similarly, the adsorption at 0.3 v and above might be assumed to occur via the secondary carbon atom. The variation of the mode of attachment of  $C_3H_8$  with potential can then be seen as essentially the attempt by the electrode to act as an electrophilic substituent to the  $C_3H_8$ . This explanation would gain in force if the potential of zero charge were in the vicinity of the changeover between the two kinds of adsorption.

An alternative explanation to account for the observations is to suggest that initial (1-site) chemisorption always occurs via the more reactive secondary carbon atom but that further (multi-site) adsorption requires the presence of high-energy adsorption sites on the Pt surface. At 0.2 v, most of these are still covered with H-atoms, at least initially. Thus, extensive 1-site adsorption occurs. Due to this 1-site adsorption, H-atoms would be displaced and, indeed, this is observed. However, by the time that this occurs there is so much  $C_3H_8$  on the electrode that it is physically impossible for the singly-bound material to revert to the triply-bonded species. At 0.3 v, according to this explanation, almost all of the required deep energy wells are available and the progress from the 1-point attachment to the 3-point attachment can proceed.

In order to test these explanations, an experiment was devised in which  $Cl^-$  ion in solution was allowed to compete for the electrode with  $C_3H_8$ . The specific adsorption of  $Cl^-$  on Pt is well known<sup>16,17</sup> and this adsorption preferentially occupies the deep energy wells on the surface. Thus, the characteristic H-atom adsorption region is depressed to lower potentials<sup>18</sup>. On this rather oversimplified model one would expect that at, say 0.3 v, where the strongly adsorbed  $Cl^-$  successfully competes for the deep wells with the  $C_3H_8$ , no deep wells will be available. If the second theory above is correct, this should lead to 1-site adsorption of  $C_3H_8$  at all potentials. On the other hand the adsorption of  $Cl^-$  clearly moves the potential of zero charge to more negative potentials and even at 0.2 v the electrode will be anodic to the point of zero charge. Then on the basis of the first theory suggested above, the adsorption of  $C_3H_8$  will occur on 3 sites even at 0.2 v.

The results of this experiment are shown in Fig. 6 for the adsorption of  $C_3H_8$  at 0.3 v and 110°C. Evidently, the normal 3-site adsorption is progressively inhibited as more HCl is added to the  $H_3PO_4$ . Also, the onset of chemisorption is considerably retarded and, as expected, the final adsorption of the  $C_3H_8$  is less than usual. In addition, it was found that at 0.2 v in the presence of 0.17 mM HCl there was no change in the adsorption kinetics. The results thus indicate that the second theory above is closest to the explanation of the variation of the mode of adsorption with potential. However, the situation is somewhat more complex than is suggested by the above theories of the effect of  $Cl^-$ . Thus, assuming that all the added HCl is dissociated (which is hardly reasonable) and that, following

Gilman<sup>18</sup>, the rate of  $\text{Cl}^-$  adsorption is limited by solution diffusion and that each adsorbed  $\text{Cl}^-$  ion occupies 1 Pt surface site, we can calculate the times at which a monolayer of  $\text{Cl}^-$  should be present on the surface of the Pt. This is shown in Fig. 6 for  $D_{\text{Cl}^-} = 2 D_{\text{C}_3\text{H}_8}$ ,

which is based on the ratio of the known value of  $D_{\text{Cl}^-}$  at 25°C in dilute solution<sup>19</sup> and the value for  $D_{\text{C}_3\text{H}_8}^{25^\circ}$  given previously. We see that particularly for the concentrated solutions of HCl the surface should be covered with  $\text{Cl}^-$  before almost any  $\text{C}_3\text{H}_8$  has been adsorbed. Thus it is difficult to see why increasing the  $\text{Cl}^-$  concentration at this stage should make any difference. The answer probably lies in the fact that in the presence of  $\text{C}_3\text{H}_8$  the  $\text{Cl}^-$  does not have the electrode all to itself and the  $\text{C}_3\text{H}_8$  can effectively compete at least for some of the sites. It is apparent that when some  $\text{Cl}^-$  is adsorbed some  $\text{C}_3\text{H}_8$  is adsorbed on 3-sites as before and some on fewer sites. Thus the slope of the  $\theta_{\text{H}}^{1/2}$  vs.  $\tau_{\text{ads}}^{1/2}$  line is decreased although the accumulation of C atoms on the surface is still governed by diffusion of  $\text{C}_3\text{H}_8$ .

Despite these difficulties, it is quite clear that the model which is favored by the experiment is the one based on the active sites' occupancy with H atoms as a function of potential and, tentatively, we can conclude that adsorption involving 3-sites occurs with greater difficulty than the initial adsorption on 1-site. From the point of view of operating a fuel cell, it is not known which of the two species, 1-site or multi-site, is the more reactive but it is clear that we can modify the mode of attachment of the  $\text{C}_3\text{H}_8$  by adding small quantities of appropriate anions to the electrolyte solution.

#### Extent of Adsorption as a Function of Temperature and Potential

In Fig. 7 we show the coverage of Pt with irreversibly adsorbed material in  $\text{C}_3\text{H}_8$ -saturated solutions as a function of potential and temperature. (Data at 80° and 110° are from ref. (1).) The data at 0.25 v or greater refer to the steady state but at lower potentials the maximum adsorption has not been reached. This is because (cf. Fig. 5) the accumulation of C atoms is very slow (1-site) at low potentials. No attempt was made to obtain the limiting coverage at these potentials since it was thought that interference from adsorption of impurities would be considerable at the long times that would be involved. For this reason, the adsorption-potential curve has been represented by a dotted line in this potential region. It is evident that  $\text{C}_3\text{H}_8$  adsorption occurs between 0.1 v and 0.7 v, with a maximum at about 0.3 v. The effect of temperature is small and within the experimental error.

The variation of the anodic charge with potential and temperature is shown in Fig. 8. The values were taken after 2 min of adsorption. Here, the data are in the steady state and it is evident that the adsorption increases rapidly from 0.1 to ~ 0.2 v and then slowly declines, becoming small or negligible at ~ 0.7 v. As before, the effect of temperature is small.

It will be seen in the next section that the correlation between the anodic and cathodic data is fairly good but we have not attempted to express the above adsorption data in the form of an isotherm related to  $C_{C_3H_8}$  since it will be made clear that the material which is finally adsorbed on the electrode is not  $C_3H_8$  as such.

#### Final Structure of "Adsorbed Propane"

It was seen earlier that the anodic and cathodic adsorbate vs.  $\tau_{ads}^{1/2}$  curves deviate from linearity after different times of adsorption. In every case, at all temperatures and potentials, the anodic charge vs.  $\tau_{ads}^{1/2}$  lines curve off first while the cathodic

curves indicate that in fact adsorption is continuing at the same rate. Previously<sup>1</sup> it was suggested that this results from the partial oxidation in the adsorbed state of the originally adsorbed material. Thus, less charge will be found in the ultimate oxidative measurement of the amount of adsorption with the anodic current pulse. This explanation fits all the observations which we presently have; for example, it accounts for the fact that the anodic charge tails off sooner at more anodic potentials and at higher temperatures. It also clearly demonstrates the dangers of attempting to characterize the adsorption in a complex system of this kind solely with anodic stripping.

If we take the limiting values of  $Q_{ads}^{C_3H_8}$  and  $\theta_H^t$ , at each potential, we can estimate the average oxidation state of the adsorbed material. The fraction of the H atom sites occupied by "adsorbed  $C_3H_8$ " is then  $(1 - \theta_H^t)$  and, when expressed in terms of the charge which would be involved in the oxidation of H atoms if they were on these  $(1 - \theta_H^t)$  sites, this corresponds to  $(1 - \theta_H^t) 210 \mu \text{ coul/cm}^2$ . Since the oxidation of each H atom involves a single electron, the ratio of the limiting values of  $Q_{ads}^{C_3H_8}$  and  $(1 - \theta_H^t) 210$  yields the average number,  $[e]$ , of electrons involved in the ultimate, high-potential oxidation of the adsorbed material per Pt surface atom which it covers. This quantity is shown as a function of potential and temperature in Fig. 9 and we see that for  $E \geq 0.3 \text{ v}$   $[e]$  is between 2 and 3 independent of temperature. The scatter is considerable as the limiting values of  $\theta_H^t$  are difficult to estimate. Below 0.3 v, the adsorbed material is in a less oxidized condition. It may be recalled that the adsorption process is still continuing at these potentials so that the data shown in the figure will be somewhat higher than the values corresponding to the adsorbate at limitingly-long adsorption times. Consequently, the remaining discussion refers to data obtained at 0.3 v and above.

$C_3H_8$  dissociatively adsorbed on 3-sites per molecule and releasing  $3H^+$  ions and 3 electrons (cf. equation (5)) should yield a material for which  $[e]$  is 5.67. Therefore, the residue found cannot be  $C_3H_8$  itself unless each adsorbed C atom is attached to about 2.8 Pt atoms (for  $[e] = 2$ ). However, we can show that this is not likely for we observe in Fig. 5 that at these potentials the rate of accumulation of C atoms is just that given by the assumption that each C atom occupies 1 Pt surface atom (3-site adsorption). This process continues even when the adsorbate is being oxidized and unless it is assumed that the C atoms re-orient on the surface some time later, when both

$\theta_H^t$  and  $Q_{ads}^{C_3H_8}$  have become constant, we may safely conclude that the adsorbed C atoms only occupy 1 Pt atom apiece. Then the observed final value of  $[e]$  plus the observation that  $[e]$  decreases during the process of adsorption suggest strongly that the adsorbate is gradually oxidized while it is on the electrode. The observation that  $[e]$  is approximately constant over a range of potentials and temperatures suggests also that this residue is just a single species whose oxidation at higher potentials involves between 2 and 3 electrons per C atom. Such a hypothesis would agree with the results of Giner<sup>20</sup> and the value 2 for  $[e]$  would recall suggestions that the final residue is something like CO (see ref. (21) for discussion of this suggestion for a similar system). However experiments we have carried out show that the composition of the adsorbate varies markedly with the potential of adsorption. This is totally unexpected from the data shown in Fig. 9.

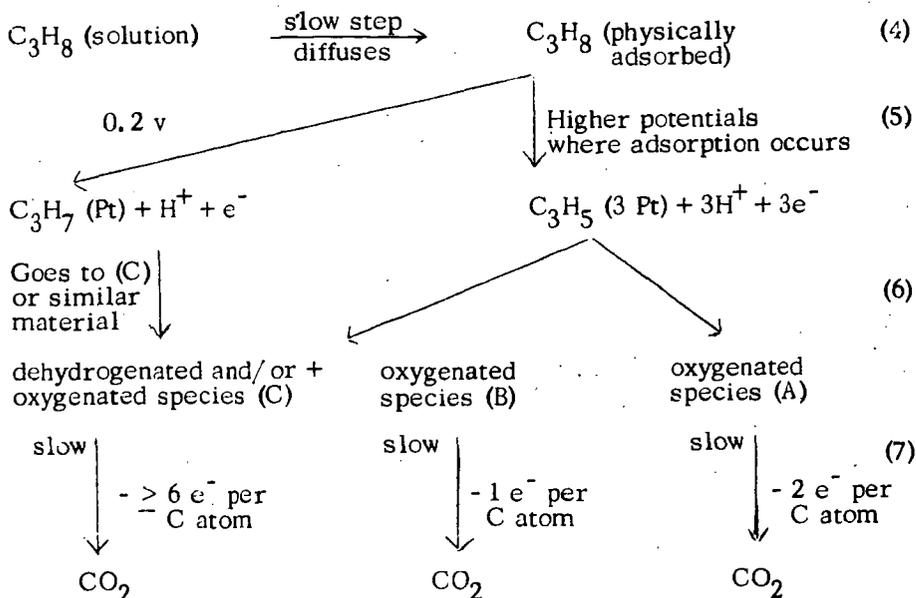
In order to trace the role played by the adsorbed intermediates in the over-all process an attempt was made to study their oxidation kinetics. The experiment consists of adsorbing material at a low potential and then displacing the potential so as to oxidize or displace the adsorbed material. A convenient potential for the latter purpose is 0.7 v, where there is insignificant oxide on the electrode to complicate the analysis. Both  $Q_{ads}^{C_3H_8}$  and  $\theta_H^t$  were followed as a function of time at 0.7 v and we find that the amount of adsorbate declines quite rapidly, becoming almost zero within 10 sec. The unexpected feature is the observation that  $Q_{ads}^{C_3H_8}$  does not follow  $(1-\theta_H^t)$  linearly with a slope corresponding to  $\sim 2$  electrons per covered Pt atom. This is shown in Fig. 10 for adsorption at  $130^\circ C$ . Here,  $\theta_{C_3H_8}$  is highest to the right of the figure and this corresponds to the condition of the adsorbate at 0.3 v. The removal of the adsorbed material is followed by tracing down the lines starting from the top right hand corner of Fig. 10. We see that most of the occupied Pt atoms are covered by a species for which  $[e]$  is  $\sim 1$ . However, the last part of the adsorbate to be removed, and hence the most difficult to oxidize, has a much higher value of  $[e]$ . The exact value of  $[e]$  in this region cannot be estimated very accurately at this time and further experiments are in progress.

However, it is clear that a fraction of the C atoms (for 100 sec at 0.3 v, these cover ~ 5% of the total surface of the electrode) are in a considerably reduced state. Because of the high state of reduction of these species they contribute a large fraction of

$Q_{ads}^{C_3H_8}$ . We cannot discriminate whether more than one such species is involved in this region, but it seems safe to hypothesize that we do not have alkyl radicals since these are presumably involved in the initial (rapid) adsorption and are then easily oxidized further. More likely, we have extensively dehydrogenated materials. For stabilization, these might involve attachment to more than 1 Pt site per C atom but this is not incompatible with the observations since only a small fraction of the C atoms would be involved.

Similar experiments on the adsorbate from 0.35 to 0.4 v (Fig. 10) show different effects. At 0.4 v, virtually all the adsorbed C atoms involve just about 2 electrons for their oxidation but at 0.35 v some of the C atoms are in a more reduced state. The increase in the amount of the more reduced (and yet harder-to-oxidize) residue with increasingly cathodic potential is expected.

These experiments demonstrate clearly the complexity of the species adsorbed on a Pt hydrocarbon anode and indicate that a careful and thoughtful approach must be used if we are to elucidate the path of the over-all reaction from  $C_3H_8$  to  $CO_2$ . Tentatively, we can suggest the following sequence for the adsorption-oxidation process:



At this time it appears from the number of electrons involved in reaction (7) that (A) may be a "CO-like" species, (B) a species similar to the formate radical and (C) is very likely a dehydrogenated species and may in fact arise from a small contribution, even at the higher potentials, from singly-bonded C atoms.

It is curious that the most highly oxidized residue (B) is found not at the highest potentials of adsorption but at an intermediate potential (0.3 v).

The distribution of these species on the electrode is demonstrably a function of potential and probably depends also on temperature and acid concentration. The description of the roles of these species in the over-all reaction is a first requirement in the understanding of the  $C_3H_8$  oxidation mechanism and further studies on their oxidation kinetics will be reported subsequently.

#### IV. CONCLUSIONS

The results of the work reported here for  $C_3H_8$  adsorption at 130 and 140°C largely confirm the previous results at 80 and 110°C<sup>1</sup> but some modification of the ideas presented earlier is required (see (5) below). The main conclusions are summarized below:

- (1) Anodic stripping yields a quantitative estimate of the amount of oxidizable material pre-adsorbed on the electrode.
- (2) The rate of adsorption is limited by diffusion in solution.
- (3) At 0.2 v, adsorption involves 1 surface site for each adsorbed molecule but at higher potentials 3 sites are used. Experiments with the addition of  $Cl^-$  indicate that this difference is related to the need for deep energy adsorption wells to convert (initial) 1-site adsorbate to 3-site attachment. It is suggested that these are covered with H atoms at 0.2 v and that this prevents significant 3-site adsorption.
- (4) The adsorbate is oxidized on the electrode and, thus, subsequent anodic stripping finds less material than expected. However, during this oxidation process, adsorption continues at the same rate and virtually none of the adsorbed and oxidizing C-atom centers is removed.

- (5) Because of this oxidation, residues whose final oxidation to  $\text{CO}_2$  is slow accumulate on the electrode surface. The oxidation of these residues may be the rate limiting step in the conversion of  $\text{C}_3\text{H}_8$  to  $\text{CO}_2$  and, at potentials more anodic than 0.3 v, appears to involve about 2 electrons per covered Pt atom independently of potential and temperature. This suggests that the same species is involved under all conditions. Desorption experiments show clearly that this is not the case and that the composition of the residue depends on the potential of adsorption.

#### ACKNOWLEDGEMENTS

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Table I. -GLOSSARY OF SYMBOLS

$C_{C_3H_8}^t$	Concentration of $C_3H_8$ at $t^\circ C$ . (moles/cm <sup>3</sup> ).
cm <sup>2</sup>	Unless otherwise stated, or in connection with $C_{C_3H_8}^t$ or $D_{C_3H_8}^t$ , refers to real area which is defined as equivalent to 210 $\mu$ coulomb for $Q_H^t$ .
$D_{C_3H_8}^t$	Diffusional coefficient of $C_3H_8$ at $t^\circ C$ (cm <sup>2</sup> /sec).
E	Potential (v. vs. reversible $H^+/H_2$ (R.H.E.)).
[e]	The average number of electrons involved in the high potential oxidation of the adsorbate per Pt atom that it covers.
F	The Faraday.
geom cm <sup>2</sup>	Geometric area of the electrode.
$i_a$	Anodic current density (amp/cm <sup>2</sup> ).
n	Number of electrons involved in oxidation of adsorbed species, see equation (3).

- $Q$  Charge ( $\mu$  coulomb/cm<sup>2</sup>).
- $Q_{dl}$  Charge due to double layer charging during anodic galvanostatic transient.
- $Q_{\text{electrode}}$  Charge due to electrode oxidation during anodic galvanostatic transient.
- $Q_H^t$  Maximum cathodic H atom charge on a clean electrode at  $t^\circ\text{C}$ .
- ( $Q_{\text{anodic}}^{\text{total}}$ )  $\text{N}_2$  Charge passed during anodic galvanostatic transient in  $\text{N}_2$ -saturated solution in potential region prior to  $\text{O}_2$ -evolution ( $\sim 0.8 - 1.8$  v depending on  $i_a$ ).
- ( $Q_{\text{anodic}}^{\text{total}}$ )  $\text{C}_3\text{H}_8$  Similar charge in  $\text{C}_3\text{H}_8$ -saturated solution.
- $Q_{\text{ads}}^{\text{C}_3\text{H}_8}$  Charge to oxidize adsorbed  $\text{C}_3\text{H}_8$ .
- $Q_{\text{diff}}^{\text{C}_3\text{H}_8}$  Charge due to oxidation of  $\text{C}_3\text{H}_8$  diffusing up to electrode during anodic galvanostatic transient.
- $S$  Number of surface sites occupied by each adsorbed  $\text{C}_3\text{H}_8$  molecule
- $t$  Temperature ( $^\circ\text{C}$ ).
- $\theta_i$  Fraction of surface covered with species  $i$ .
- $\theta_H^t$  Ratio of the H atom charge under a given circumstance to the maximum value at the same temperature.
- $\tau$  Time (sec).
- $\tau_{\text{ads}}$  Time of adsorption.
- $\tau_E$  Time at potential  $E$ .
- $\tau_H$  Transition time during measurement of  $Q_H^t$  by galvanostatic pulse.

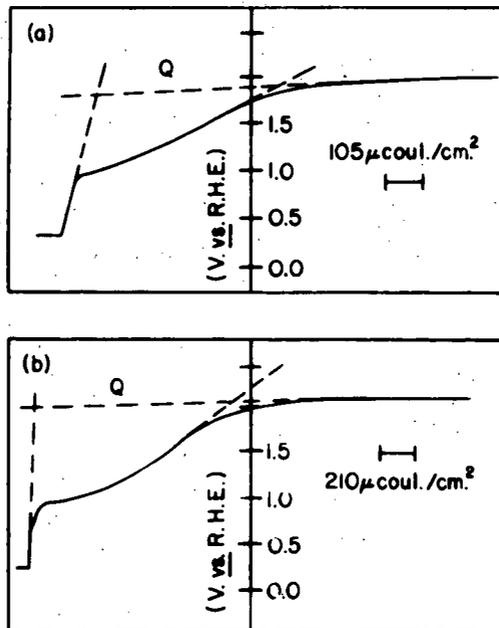
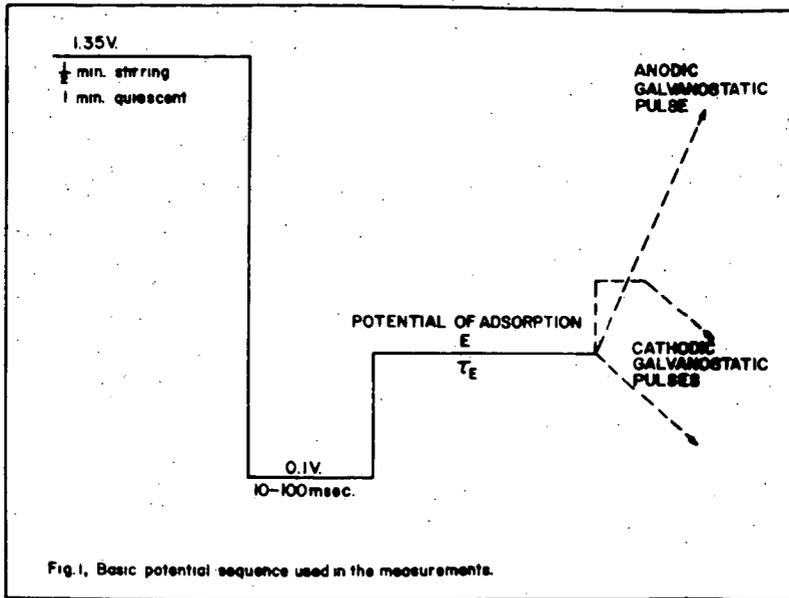


Fig. 2. Typical anodic charging curves at  $130^\circ\text{C}$  in presence of  $\text{C}_3\text{H}_8$ . Curves were taken at  $114 \text{mA./cm.}^2$   
 (a) after 10 msec., (b) after 2 min. at 0.3V.

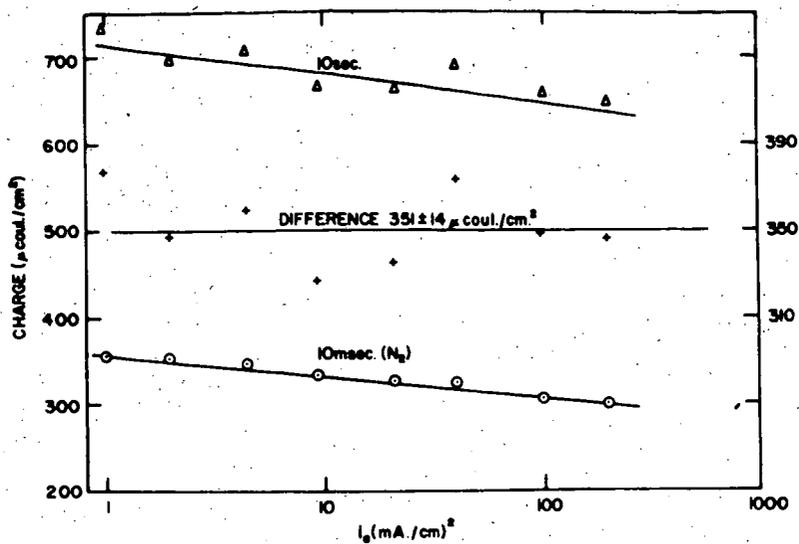


Fig. 3. Adsorption of  $\text{C}_3\text{H}_8$  at 0.3V and 130°C.  $\Delta$ ,  $(Q_{\text{ads.}}^{\text{total}})_{\text{C}_3\text{H}_8}$  after 10 sec.  
 $O$ ,  $(Q_{\text{ads.}}^{\text{total}})_{\text{N}_2}$  after 10 sec.  $+$ , DIFFERENCE =  $Q_{\text{ads.}}^{\text{C}_3\text{H}_8} - Q_{\text{ads.}}^{\text{N}_2}$

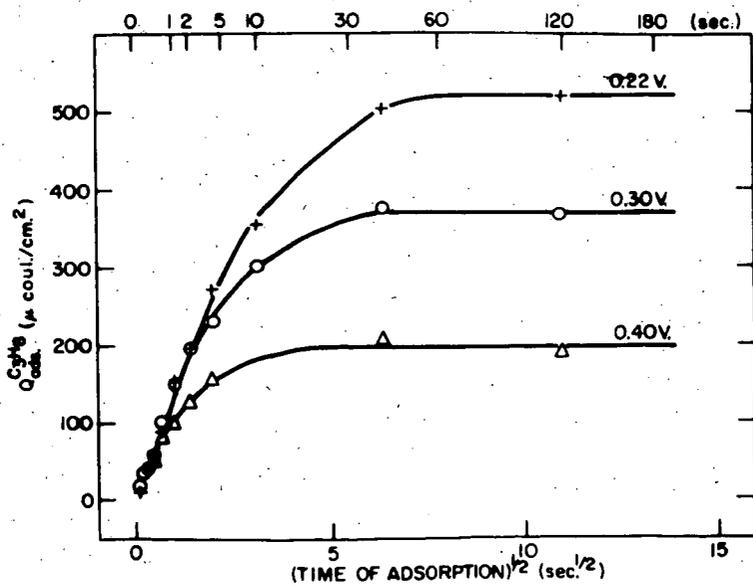


Fig. 4. Variation of  $Q_{\text{ads.}}^{\text{C}_3\text{H}_8}$  with  $T_{\text{ads.}}^{1/2}$  at 130°C.

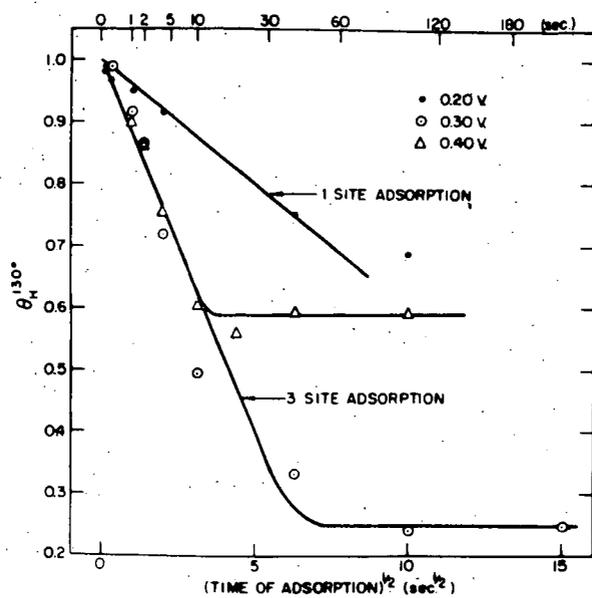


Fig. 5. Variation of  $\theta_H$  with  $\tau_{ads}^{1/2}$  at  $130^\circ\text{C}$ .

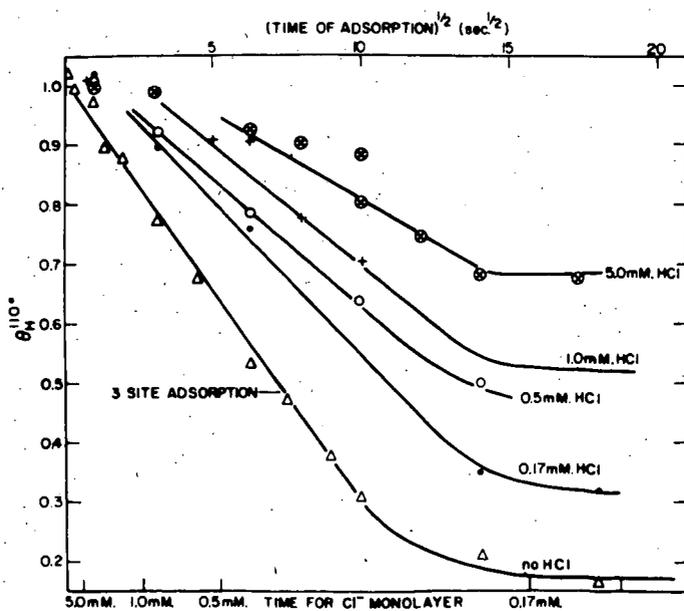


Fig. 6. Variation of  $\theta_H^{110^\circ}$  with  $\tau_{ads}^{1/2}$  at  $0.3\text{V}$ , in presence of  $\text{HCl}$ .

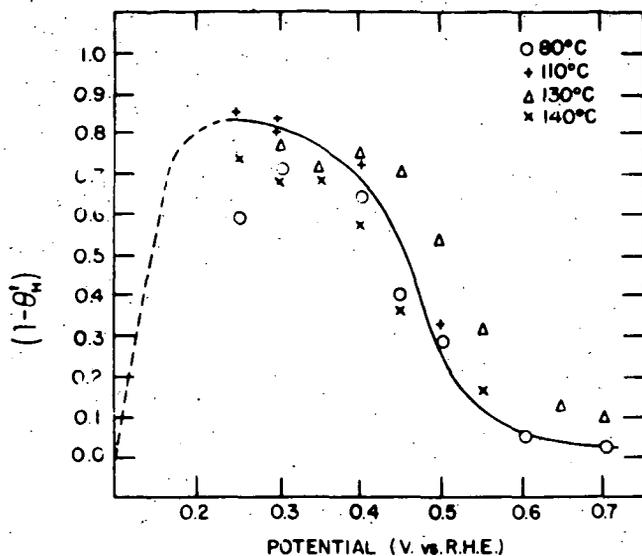


Fig. 7. Coverage of Pt with irreversibly adsorbed material as a function of potential and temperature.

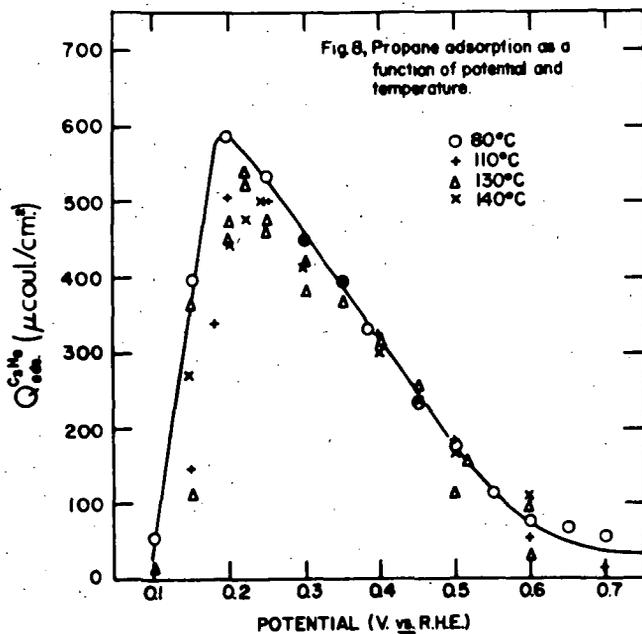


Fig. 8. Propane adsorption as a function of potential and temperature.

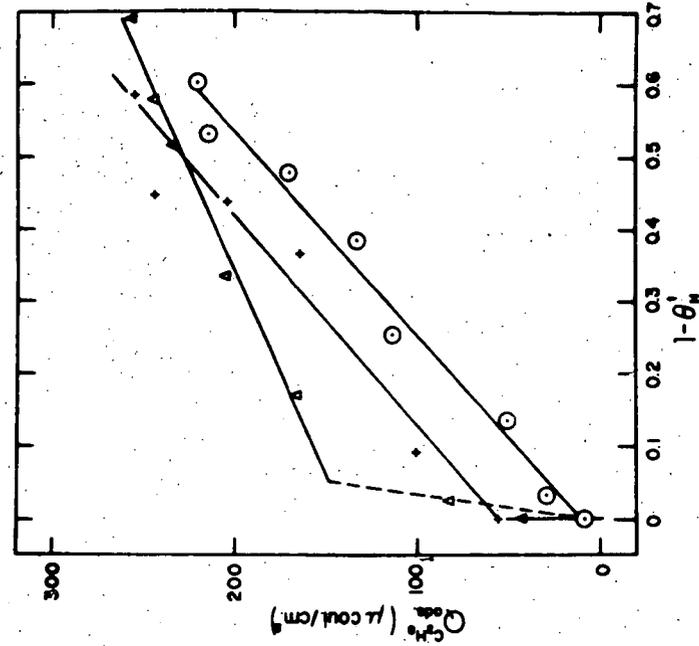


Fig. 10. Variation of the anodic charge with electrode coverage during desorption of 0.7V of material adsorbed at 130°C. Adsorption at 0.4V for 60sec; ○; 0.35V for 60sec; ◊; 0.3V for 100sec. Δ.

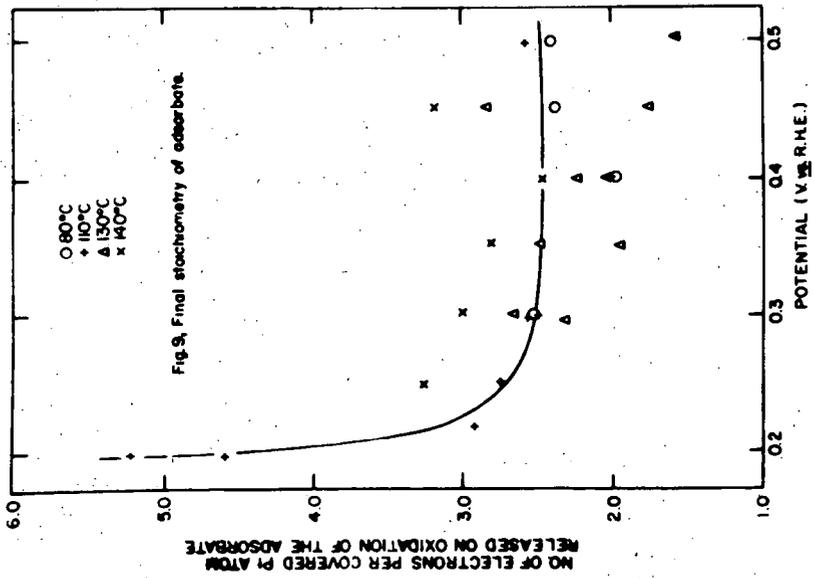


Fig. 9. Final stoichiometry of adsorbate.