

# The Vanadium Pentoxide–Titanium Dioxide System

## Part 2. Oxidation of *o*-Xylene on a Monolayer Catalyst<sup>1</sup>

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Hydroxyl groups on the surface of anatase react with the vapor of  $\text{VOCl}_3$  at room temperature to give a partial monolayer of a vanadium species which after heating to 670 K is active for the oxidation of *o*-xylene. Rehydroxylation by  $\text{H}_2\text{O}$  followed by outgassing at 410 K and further treatment with  $\text{VOCl}_3$  leads to improved catalytic properties, and after six such cycles a monolayer catalyst is produced which contains 1.7%  $\text{V}_2\text{O}_5$  and which is superior even to a doubly promoted catalyst prepared by conventional impregnation. Below about 600 K, however, the carbon mass balance shows that not all the *o*-xylene fed to the reactor is recovered as volatile products. The missing carbon is at least partly in the form of a surface deposit which is thought to be responsible for initial losses of activity: these have been followed at various temperatures and flow rates. The carbon in this surface deposit has been quantitatively estimated by oxidation to  $\text{CO}_2$ , the results indicating that below about 560 K the deposit covers most of the surface. The kinetics of the reaction have been studied at 582 and 608–610 K. At both temperatures the process of carbon loss increases with *o*-xylene pressure, causing maxima in the rate of *o*-xylene conversion, and is suppressed by increasing oxygen pressure: the conversion varies as the square root of the oxygen pressure. A model is developed in which chemisorbed oxygen atoms doubly bonded to  $\text{V}^{5+}$  ions are the oxidizing species. If *o*-xylene adsorbs by dissociation of a hydrogen atom from a single methyl group at an uncovered site, its further oxidation to phthalic anhydride proceeds smoothly. If, however, by interaction with another uncovered site a hydrogen atom is lost from the second methyl group, a strongly adsorbed species is formed which constitutes or is the precursor to the surface deposit.

### INTRODUCTION

Oxidation of *o*-xylene is the major industrial process for the production of phthalic anhydride, and for this reason the reaction has been extensively studied in recent years (1–3). Catalysts for this process always contain  $\text{V}_2\text{O}_5$  as the active component, and of the various supports examined  $\text{TiO}_2$  has proved to be the most effective (4, 5). Products beside phthalic anhydride include *o*-tolualdehyde, *o*-toluic acid, phthalide, together with minor amounts of maleic anhydride, and the products of total

combustion, CO and  $\text{CO}_2$ , which even with the most selective catalysts account for 20–25% of the reacted *o*-xylene. Kinetic studies (6, 7) indicate that the products are formed through a complex consecutive-parallel scheme, with *o*-tolualdehyde as the primary product. Nonselective oxidation has been attributed to the presence of acidic surface sites (6) at which the electron-rich benzene ring may form strongly bound hydrocarbon residues which are only oxidized to carbon oxides (8).

The reasons for the peculiar efficacy of  $\text{TiO}_2$  as a support for  $\text{V}_2\text{O}_5$  have not yet been satisfactorily explained, although they may be connected with the close structural similarities between  $\text{V}_2\text{O}_5$  (and lower oxides) and  $\text{TiO}_2$  noted by Vējux and Courtine (9). If there were some epitaxial effect of

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the  $\text{TiO}_2$  surface upon a  $\text{V}_2\text{O}_5$  layer in intimate contact with it, optimum catalytic performance would be expected when the coverage of the support by  $\text{V}_2\text{O}_5$  is complete but the layer of  $\text{V}_2\text{O}_5$  rather thin. Indeed the optimum  $\text{V}_2\text{O}_5$  content lies between 2 and 10 mol%, equivalent to 1 to 5 monolayers (10). The literature reveals a number of methods for producing thin monomolecular layers of oxides on the surface of supports bearing hydroxyl groups (11–14): the term monolayer catalyst is now employed to describe such materials. One of the methods for their preparation involves specific chemical reaction between surface hydroxyls and a chloro-compound of a metal, and the reaction may be conducted either in solution (13) or in the vapor phase (11, 14). We have prepared a series of catalysts having various fractions of a  $\text{V}_2\text{O}_5$  monolayer on anatase by vapor-phase reaction of  $\text{VOCl}_3$  with water chemisorbed on the surface. The method and the properties of these catalysts are described below.

There is little information on the forms of oxygen involved in the oxidation of *o*-xylene, or on the optimum oxidation state of the vanadium ions. The participation of lattice oxygen in selective oxidations (15) is a rather general phenomenon and indeed the oxidation of butadiene to maleic anhydride on  $\text{V}_2\text{O}_5$ - $\text{TiO}_2$  catalysts proceeds in this way (16). There is a great deal of evidence (17–20) to show that  $\text{V}_2\text{O}_5$  when used as a selective oxidation catalyst undergoes a partial reduction, e.g., to  $\text{V}_6\text{O}_{13}$  (21), although at sufficiently high temperatures  $\text{V}^{4+}$  ions can diffuse into the  $\text{TiO}_2$  lattice (19, 20), thereby catalyzing the anatase to rutile transformation (9, 16).

The chief purposes of this work were twofold: first, to investigate the effect on catalytic properties of increasing the coverage of the anatase surface by a thin  $\text{V}_2\text{O}_5$  layer; and second, with the monolayer catalyst to obtain more detailed information on the mechanism of the reaction. Some novel and unexpected results have been obtained in the course of this investigation.

## EXPERIMENTAL

**Catalyst Preparation.** The same batch of anatase (Tioxide International) was used for all preparations: its chemical and physical properties are given in Table 1.

Monolayer catalysts were prepared *in situ* in a Pyrex U-tube of 0.5 cm. The first experiment was designed to find out whether  $\text{VOCl}_3$  could react with a substantially dehydroxylated surface. Anatase (0.5 g, bed length 1.5 cm) was first placed in one arm of the tube between silica wool plugs, and then heated at 720 K for 3 h in a stream of dry air. After cooling to room temperature, the air flow was diverted through a trap containing silica wool wetted with 0.5 ml  $\text{VOCl}_3$  (Ventron, reagent grade) at 293 K. After overnight treatment the reactor was slowly raised to 670 K while continuing the flow of dry air, to remove excess  $\text{VOCl}_3$  from the catalyst. The first set of catalytic measurements was then performed. The vanadium content of this catalyst was 0.71% as  $\text{V}_2\text{O}_5$ .

In order to build up the  $\text{V}_2\text{O}_5$  monolayer, the same material was then treated with moist air at 323 K (2 h,  $20 \text{ cm}^3 \text{ min}^{-1}$ ,  $P_{\text{H}_2\text{O}}$  200 Torr) to rehydroxylate the uncovered anatase surface. After heating in dry air at 413 K for 4 h to remove physically adsorbed water, the reactor was cooled to room temperature and the  $\text{VOCl}_3$  treatment applied exactly as before. A further set of catalytic measurements was then made, and the whole cycle of water and  $\text{VOCl}_3$  treatments followed by assessment of catalytic behavior was repeated a number of times. No further change in behavior was produced by the sixth treatment, after which the  $\text{V}_2\text{O}_5$  content was 1.74 wt%. Most of the work reported in this paper was performed on this last catalyst.

For purposes of comparison, two other catalysts were prepared by an impregnation procedure, as follows.  $\text{V}_2\text{O}_5$  (1 g) and oxalic acid (3.5 g) were dissolved in 15 ml water: after filtering the dark blue solution, and adding optional promoters, anatase (10 g)

was introduced, and the resultant slurry evaporated over a steam bath with continuous stirring until a thick paste was obtained. This was then dried overnight at 393 K and calcined for 6 h at 720 K, followed by crushing and sieving: the 150- to 250- $\mu$ m fraction was used as the catalyst.

*Catalytic measurements.* *o*-Xylene oxidation was performed in a conventional flow apparatus at 1 atm pressure. Catalysts prepared by impregnation were placed in the reactor in the same way as was the anatase used for making the monolayer catalysts, described above. Most experiments used a reactant mixture made by saturating air with *o*-xylene vapor at 290.0 K: this contained 0.54 mol% *o*-xylene. When investigating orders of reaction with respect to *o*-xylene, the temperature of the saturation unit, consisting of two traps in series, was adjusted to give the desired partial pressure. The oxygen content of the reaction mixture was altered by blending either oxygen or nitrogen with the air. All gases were passed through purifying towers containing "Carbosorb" and 5A and 13X molecular sieves in series. When necessary, rates were calculated from feed rates and conversion.

The outlet tube from the reactor was maintained at 443 K to prevent condensation of high-boiling products, and led into the oven of the gas chromatograph (Perkin Elmer F11), also held at 443 K. The sampling valve (0.2 cm<sup>3</sup> capacity) was also mounted in the oven. The exit stream passed through a trap at 195 K by which condensable products were held, and then

through a bed of 4% Pd/anatase catalyst (1  $\times$  5 cm) at 530 K to convert CO into CO<sub>2</sub>. The final CO<sub>2</sub> concentration was measured by a constant-dispersion ir gas analyzer (Grubb Parsons IRGA 20).

Products were separated on a 3 m column of 20% silicone 550 on 60-100 mesh Chromosorb W, with N<sub>2</sub> at 15.5 cm<sup>3</sup> min<sup>-1</sup> as carrier gas, at a constant temperature of 443 K, and were sensed by an FID detector. Under these conditions retention times relative to *o*-xylene were: *o*-tolualdehyde, 1.67; *o*-toluic acid, 3.41; phthalic anhydride, 3.86; and phthalide, 4.51. Maleic anhydride appeared just before the *o*-xylene peak, and traces of benzene and toluene appeared close to the air peak. Amounts of *o*-toluic acid were always extremely small and are not recorded in the analyses.

Unless otherwise stated, quoted values of conversion and selectivity pertain to steady-state conditions on a catalyst which had been operating for at least 8 h previously.

## RESULTS

### *Vanadium Content of Monolayer Catalyst*

Roozeboom *et al.* (12) define  $\phi_{\text{VO}_{2.5}}$  as the average area of support surface which one VO<sub>2.5</sub> unit occupies. For bulk V<sub>2</sub>O<sub>5</sub>, its value is about 0.105 nm<sup>2</sup>. After one treatment of anatase by VOCl<sub>3</sub>, the observed V<sub>2</sub>O<sub>5</sub> content of 0.71 wt% corresponds to a value of  $\phi_{\text{VO}_{2.5}}$  of 0.21 nm<sup>2</sup> which is about the same as that observed when treating anatase with a solution of ammonium vanadate acidified to pH 4 with HNO<sub>3</sub> (12). However the six treatments alternately with water and VOCl<sub>3</sub> described above gave a V<sub>2</sub>O<sub>5</sub> content of 1.74 wt%, for which  $\phi_{\text{VO}_{2.5}}$  is 0.090 nm<sup>2</sup>; this is close to the value of  $\sim$ 0.105 nm<sup>2</sup> calculated for bulk V<sub>2</sub>O<sub>5</sub>, and is evidence that the final catalyst prepared by repeated water and VOCl<sub>3</sub> treatments comprised essentially a monolayer of V<sub>2</sub>O<sub>5</sub> on the anatase surface.

TABLE I

Physical Properties and Chemical Composition of Anatase Support

Surface area, 9.8 m <sup>2</sup> g <sup>-1</sup>	P <sub>2</sub> O <sub>5</sub> , 0.45% w/w
Crystallite size, >150 nm	SO <sub>3</sub> <sup>2-</sup> , 0.02% w/w
Particle size, 150-250 $\mu$ m	K <sub>2</sub> O, 0.28% w/w
Phase, mainly anatase (0.5% rutile)	Na <sub>2</sub> O, 0.03% w/w

*Variation of Product Selectivities with Temperature for Monolayer and Impregnation Catalysts*

The effect of temperature on conversion and product distribution was determined under standard conditions using the 1.7%  $V_2O_5$  monolayer catalyst between 525 and 635 K: the results are presented as Arrhenius plots in Fig. 1 (conversion, and selectivities for phthalic anhydride (PA), *o*-tolualdehyde (TAL), and phthalide (PL), and their sum) and in Fig. 2 (selectivity for  $CO_2$ ). These results are of a similar form to those reported by other workers for  $V_2O_5$ - $TiO_2$  catalysts (5, 6). The most significant features are the following: at the low conversions observed at the lower temperatures, substantial amounts of *o*-tolualdehyde and phthalide are formed, but the

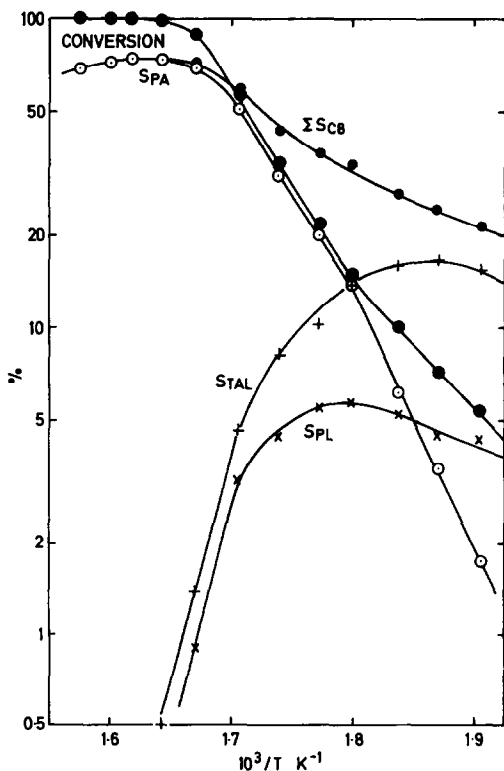


Fig. 1. Arrhenius plots of dependence of conversion and of product selectivities ( $S_{PA}$ ,  $S_{TAL}$ , and  $S_{PL}$ ) on temperature for the 1.7%  $V_2O_5$  monolayer catalyst. ●, Conversion; ○,  $S_{PA}$ ; ●,  $\Sigma S_{CB}$ ; ×,  $S_{PL}$ ; +,  $S_{TAL}$ .

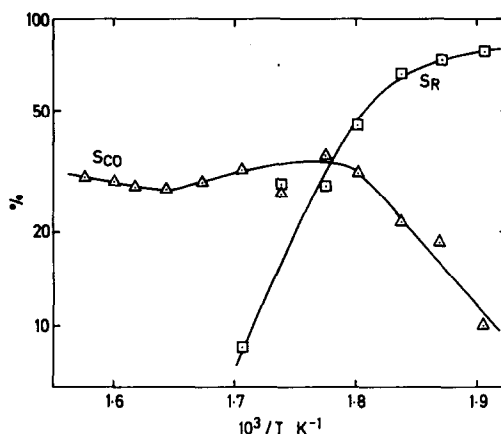


Fig. 2. Arrhenius plots of dependence of product selectivities ( $S_{CO}$  and  $S_R$ ) on temperature for the 1.7%  $V_2O_5$  monolayer catalyst. △,  $S_{CO}$ ; □,  $S_R$ .

amounts tend to zero as the conversion approaches 100%. The selectivity for phthalic anhydride increases with conversion and temperature to a maximum of about 75% at 610 K, thereafter decreasing slightly due to further oxidation to  $CO_2$ . The activation energy based on *o*-xylene removal was 115  $kJ\ mol^{-1}$ . Activation energies should not of course strictly be derived, as this value was, from the temperature dependence of conversion, but from the rate coefficients: however, it follows from the definition of rate coefficient that its proper value and dimensions depend on the orders of reaction, whose variation with temperature is rarely measured. The whole concept of activation energy in heterogeneously catalyzed reactions is thus brought into question (22); we therefore are content, as many other workers are, to quote values derived from the temperature dependence of conversion, while recognizing the limited significance of the actual number.

Similar sets of results were obtained with the two catalysts prepared by impregnation with the same anatase: one contained 10% w/w  $V_2O_5$  and the other 10%  $V_2O_5$ , 2%  $P_2O_5$ , and 2%  $Rb_2O$  (all nominal w/w). The unpromoted catalyst had a similar activity and activation energy (120  $kJ\ mol^{-1}$ ) to the monolayer catalyst, but the doubly pro-

TABLE 2

Comparison of Product Selectivities Given by the Monolayer Catalyst with Those for Unpromoted and Doubly Promoted Impregnation Catalysts at Different Conversions

	<i>T</i> (K)	<i>S</i> <sub>TAL</sub>	<i>S</i> <sub>PL</sub>	<i>S</i> <sub>PA</sub>	<i>S</i> <sub>CO<sub>2</sub></sub>	Σ <i>S</i> <sub><i>i</i></sub>
20% conversion						
Monolayer catalyst	563	11.7	5.6	18.5	34.7	70.5
Unpromoted impregnation catalyst	555	9.9	5.5	20.0	28.2	63.6
Doubly promoted catalyst	557	13.6	8.3	14.3	27.2	63.4
50% conversion						
Monolayer catalyst	584	5.5	3.5	45.2	31.0	85.2
Unpromoted impregnation catalyst	578	4.4	2.5	49.5	22.6	79.0
Doubly promoted catalyst	572	6.7	6.0	35.1	25.8	73.6
99% conversion						
Monolayer catalyst	611	0.4	0.2	75.0	24.7	100.3
Unpromoted impregnation catalyst	606	0.4	<0.1	64.6	29.2	94.3
Doubly promoted catalyst	585	0.6	0.3	67.9	26.9	95.7

moted one, showing a higher activation energy of 166 kJ mol<sup>-1</sup>, was significantly more active at higher temperatures. In Table 2 the product selectivities for the three catalysts are compared at 20, 50, and 99% conversion: these selectivities are defined as moles of product detected (or for CO<sub>2</sub>, moles × 1/8) per mole of *o*-xylene reacted. Maximum yields of phthalic anhydride and the temperatures at which these occurred were, for the monolayer catalyst, 103 g/100 g *o*-xylene (616 K); for the unpromoted impregnation catalyst, 89 g (610 K); and for the doubly promoted catalyst, 94 g (592 K). The monolayer catalyst thus exhibits distinctly a higher yield and selectivity for phthalic anhydride at high conversion than the other catalysts.

However, in almost every case the sum of the selectivities for the major products (Σ*S*<sub>*i*</sub> in Table 2) is less than 100%: the accuracy of the analysis allows an uncertainty in this quantity of only about ±5%. The observed discrepancy is usually much greater than this, especially at low temperatures and low conversions. Figure 2 shows the carbon deficit (defined as *S*<sub>R</sub>, the number of moles of *o*-xylene not detected as other products per mole of *o*-xylene fed) for the

monolayer catalyst as a function of reciprocal temperature.

The carbon deficit evidently shows a similar trend to the intermediates (Fig. 1). It must be emphasized that these carbon losses are observed while catalysts are functioning in a steady state, that is, without measurable change in activity in the 30-min period preceding the reported analysis.

#### *Initial Transient Changes under Standard Conditions with the Monolayer Catalyst*

In order to monitor the changes in catalytic activity during the initial transient period before a steady behavior is obtained, the monolayer catalyst was oxidized in air at 680 K for 1 h (although usually no more CO<sub>2</sub> was evolved after the first 10 min), allowed to cool to the chosen reaction temperature, and then the air flow diverted through the *o*-xylene saturators. The total flow rate was 32.4 cm<sup>3</sup> STP min<sup>-1</sup>. Samples were analysed at 10-min intervals, and the results obtained at 614, 588, 566, and 536 K are shown in Fig. 3. Another set of results was obtained at 557 K, but they were similar to those at 566 K and are therefore not shown. The matter for immediate comment is that conversion decreases with time *ex-*

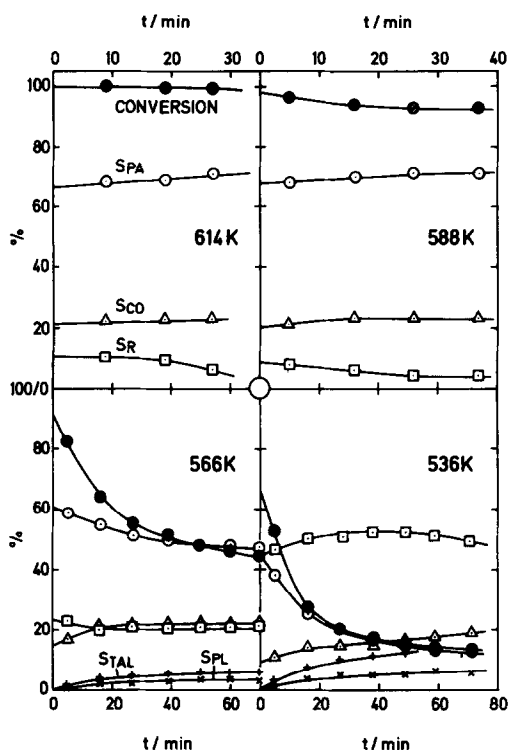


Fig. 3. Transient changes in conversion and product selectivities at 614, 588, 566, and 536 K. Symbols as in Figs. 1 and 2.

cept at the highest temperature, and the rate of decrease (as measured for example by the change of conversion during the first 20 min) grows larger as the temperature is lowered. At the same time the selectivity for carbon loss  $S_R$  becomes greater. In Fig. 4 we plot the fractional conversion decrease in the first 20 min as a function of  $S_R$ , taking both the initial and subsequent maximum or minimum values, and find a satisfactory correlation. At the two higher temperatures the carbon loss is initially greater than the steady-state value: indeed Table 2 shows that its value at 611 K is close to zero. The observed changes in the other product selectivities are broadly as expected from the changes in conversion; only the progressive increase in  $S_{CO}$  at 536 K is unexpected. Initial loss of activity has been observed before (5), but was then ascribed to reduction of the catalyst.

To obtain further information on this matter, we followed the initial changes in conversion and product selectivities at constant temperature (533 K) with three different total reactant flow rates (21.8, 33.6, and  $60.9 \text{ cm}^3 \text{ min}^{-1}$ ) but with an *o*-xylene partial pressure of 0.13 mol% instead of the normal 0.54%. This was with the purpose of lengthening the time scale over which the transient changes were expected to occur. The results are shown in Fig. 5. The use of lower *o*-xylene concentration results in initial values of  $S_R$  lower than those shown in Fig. 3, in conformity with further observations described below. We note that the rate of decrease of conversion declines with decreasing flow rate and that this is accompanied by a lowering of the selectivity for carbon loss  $S_R$ . The fractional conversion decrease up to 20 min is also plotted against  $S_R$  in Fig. 4 (its minimum value in the case of the slowest flow rate) and the points are consistent with those obtained by temperature variation, confirming the connection between deactivation and carbon deficit.

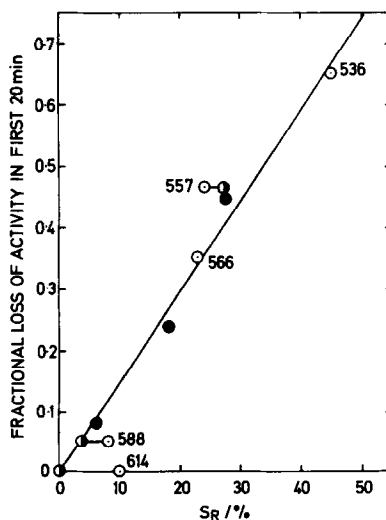


Fig. 4. Dependence of fractional decrease in activity in first 20 min on stream upon the value of  $S_R$ .  $\circ$ , Initial value of  $S_R$  from temperature variation.  $\bullet$ , Steady-state value of  $S_R$  from temperature variation (temperatures are given by the points).  $\circ$ , Steady state or minimum value of  $S_R$  from flow rate variation at 533 K.

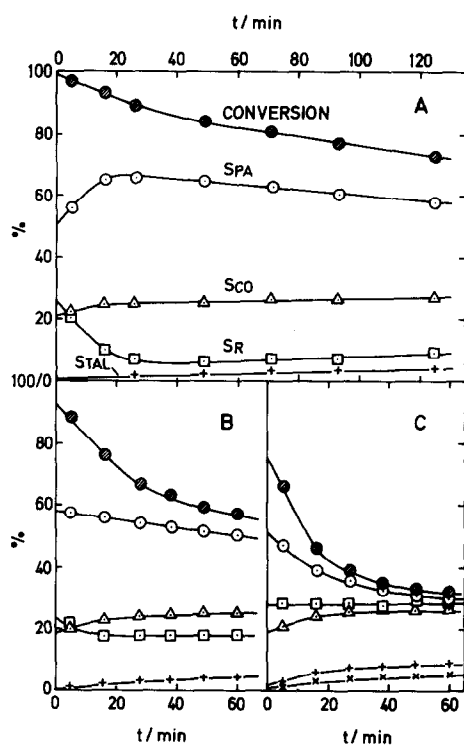


Fig. 5. Transient changes in conversion and product selectivities at 533 K using 0.13 mol% *o*-xylene in air and various flow rates. (A) 21.9 cm<sup>3</sup> min<sup>-1</sup>; (B) 33.6 cm<sup>3</sup> min<sup>-1</sup>; (C) 60.9 cm<sup>3</sup> min<sup>-1</sup>. Symbols as in Figs. 1 and 2. Traces of phthalide were found at the lower flow rates (<1% in A, <3% in B), but the results are omitted for clarity.

The changes in the other product selectivities are again consistent with the changes in conversion, although  $S_{CO}$  consistently rises, as we saw earlier.

#### The Nature of the Missing Carbon

From the foregoing results it was strongly suspected that the carbon loss observed during the initial transient phase was at least partly if not wholly retained on the catalyst surface in the form of a strongly held carbonaceous deposit. To investigate this further we interrupted a steady-state reaction by diverting the air flow from the *o*-xylene saturators, and observed the way in which the CO<sub>2</sub> concentration varied with time: some of the results are shown in Fig. 6. At the highest temperature (618 K) the CO<sub>2</sub> concentration falls abruptly on stopping the *o*-xylene flow, whereas at the lowest temperature used (568 K) CO<sub>2</sub> continued to be evolved in easily measurable amounts for more than 2 h, in the manner shown. We attribute the further formation of CO<sub>2</sub> to oxidation of the carbonaceous deposit. Integration of the area under the curve during the isothermal oxidation of the deposit ( $A_1$ ) does not however give the total amount of oxidizable carbon, for if when

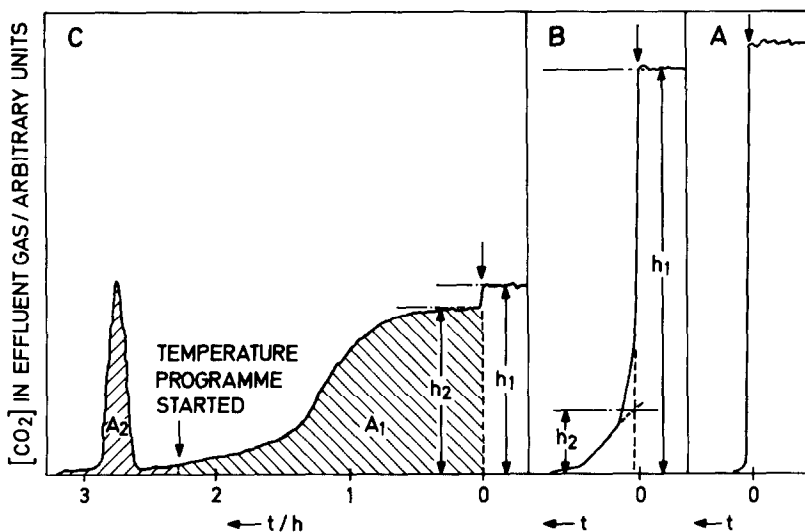


Fig. 6. Variation in CO<sub>2</sub> content of effluent gas with time after stopping the *o*-xylene flow at various temperatures. (A) 618 K; (B) 604 K; (C) 568 K.

the  $\text{CO}_2$  concentration has fallen below the limit of detection the temperature is linearly increased, a further amount of  $\text{CO}_2$  is evolved (area  $A_2$ ). The latter is not however more than 10% of  $A_1$  at any temperature. If now we designate  $h_2$  as the concentration of  $\text{CO}_2$  at the beginning of the oxidation of the carbonaceous deposit and  $h_1$  as the steady state level (see Fig. 6), then the ratio  $h_2/h_1$  may be taken as a measure of the fraction of  $\text{CO}_2$  formed by oxidation of the deposit *in the steady state*. This ratio, and the total carbon oxidized (viz.  $A_1 + A_2$ ), were measured at a number of temperatures and the results are shown in Fig. 7. The low-temperature limit of total carbon is seen to lie in the vicinity of that calculated for monolayer coverage of the catalyst by carbon, the area per carbon atom being taken as one-sixth of the area of a benzene molecule, i.e., 0.13  $\text{nm}^2$ . The quantity of carbon in the surface deposit falls very steeply with increasing temperature between about 560 and 600 K, which is the region in which conversion increases from less than 20 to almost 100% (Fig. 1).

#### Kinetics of *o*-Xylene Oxidation on the Monolayer Catalyst

We have investigated the effect of the variation separately of the *o*-xylene ( $P_X$ )

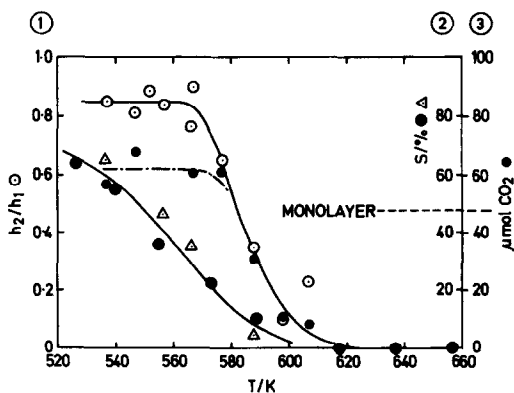


Fig. 7. Temperature dependence of  $h_2/h_1$  (○, scale 1) (see text and Fig. 6) and of quantity of  $\text{CO}_2$  released on oxidation of surface deposit (●, scale 3). Initial (Δ) and steady state (◻) values of  $S_R$  from Figs. 3 and 1, respectively, are shown for comparison (scale 2).

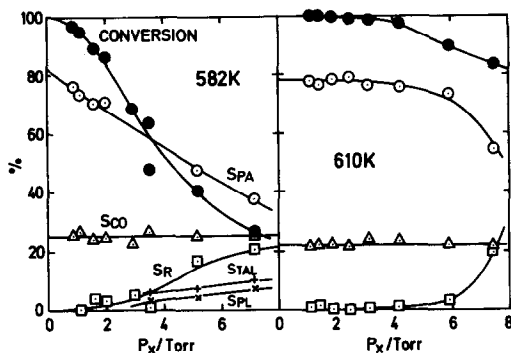


Fig. 8. Dependence of conversion and of product selectivities upon *o*-xylene pressure ( $P_X$ ) at 582 and 610 K. Symbols as in Figs. 1 and 2.

and oxygen ( $P_O$ ) partial pressures on conversion and product distribution at 582 and 608–610 K using the monolayer catalyst. Figure 8 shows the dependence of conversion and selectivities on  $P_X$ , and Fig. 9 the variation of the corresponding rates on  $P_X$ , at these temperatures, the rates being based (for easier comparison) on the carbon content of each product, i.e., as  $\mu\text{g at. C min}^{-1}$ : thus for  $\text{C}_8$  products this is eight times the rate in  $\mu\text{mol min}^{-1}$ . Up to about 4 Torr at 610 K and up to about 1 Torr at 582 K, conversions exceed 95% and rates of formation of phthalic anhydride and of carbon oxides are proportional to  $P_X$ . Above these values the loss of carbon becomes evident

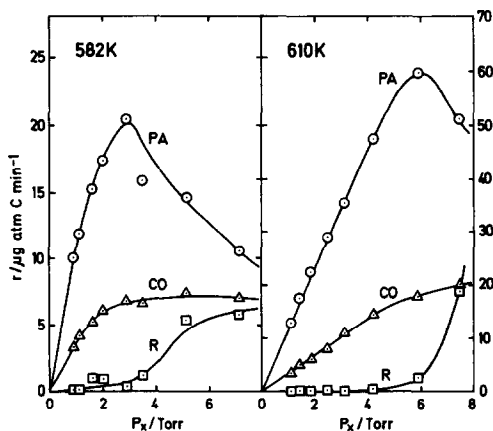


Fig. 9. Dependence of rates of product formation upon *o*-xylene pressure ( $P_X$ ) at 582 and 610 K. Symbols as in Figs. 1 and 2.



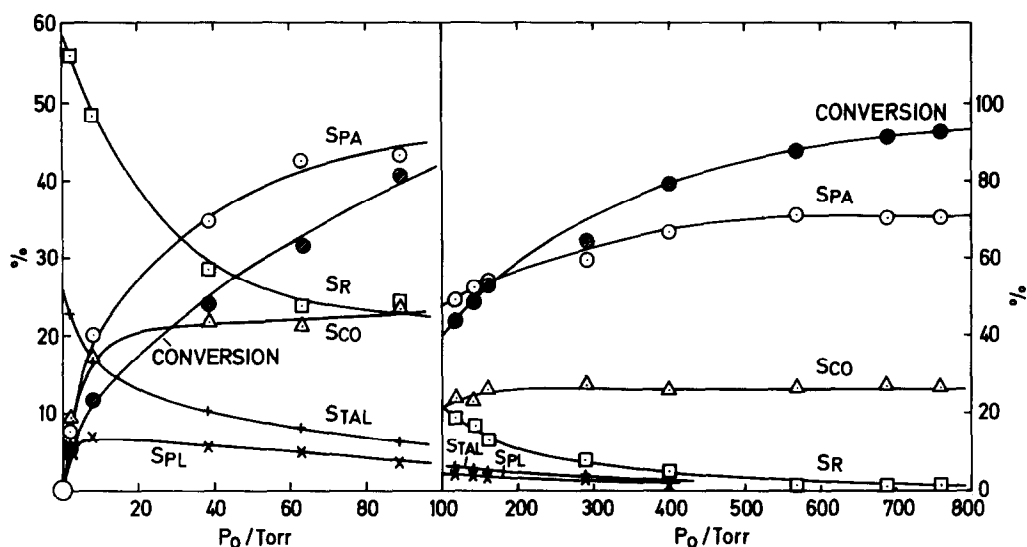


Fig. 10. Dependence of conversion and product selectivities upon oxygen pressure ( $P_O$ ) at 582 K. Symbols as in Figs. 1 and 2.

and simultaneously the conversion falls and the rate of phthalic anhydride formation passes through a maximum (3 Torr at 582 K, 6 Torr at 610 K).

The effect of varying  $P_O$  was also examined (582 K, 2–760 Torr; 608 K, 12–745 Torr). The changes in conversion and product selectivities are shown in Figs. 10 and 11; conversions and rates of carbon oxides formation are plotted against  $P_O^{1/2}$  in Fig. 12. Particularly noteworthy are the high values

of  $S_R$  (~60%) as  $P_O$  tends to zero at both temperatures, and the high value of  $S_{TAL}$  (~25%) as  $P_O$  falls to zero at 582 K, in confirmation of previous observations (6, 7). The results yield the following orders in  $P_O$ : for total C<sub>8</sub> product formation, 0.62 at 582 K and 0.69 at 608 K; for carbon deposit formation, ~0.2 at 582 K and ~0 at 608 K.

Further inspection of the results reveals that at each temperature the product composition depends only upon the conversion,

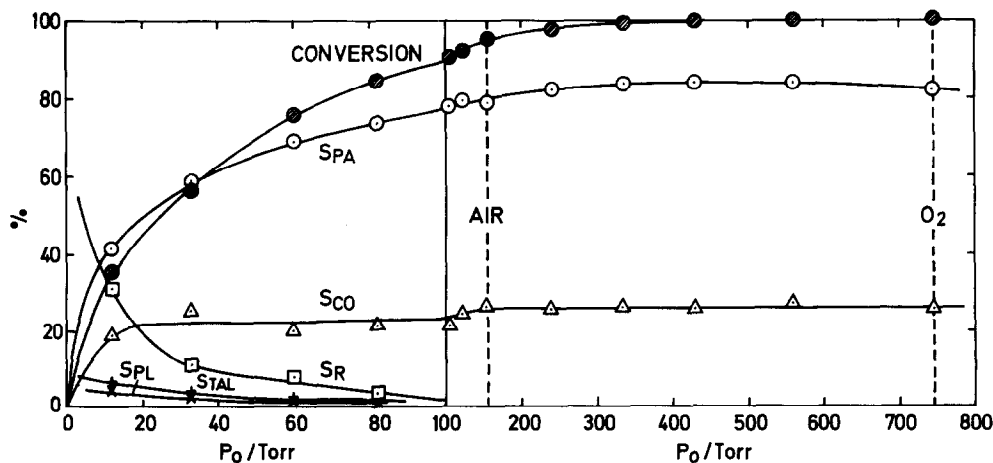


Fig. 11. Dependence of conversion and product selectivities upon oxygen pressure ( $P_O$ ) at 608 K. Symbols as in Figs. 1 and 2.

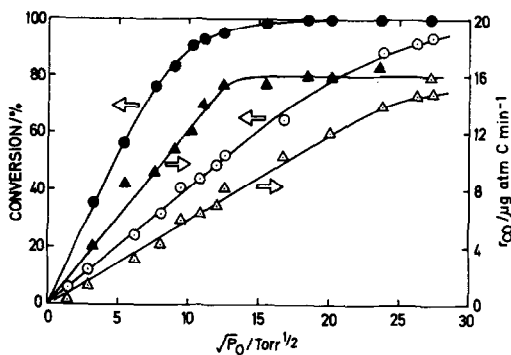


Fig. 12. Dependence of conversion and of rate of carbon oxides formation upon  $P_{O^1}$ . Open points, 582 K; hatched points, 608 K.

regardless of whether this is varied by changing  $P_X$  or  $P_O$ . A selection of selectivities obtained at 582 K is plotted as a function of conversion in Fig. 13: the close concordance between the effects of varying  $P_O$  and  $P_X$  is evident.

#### Behavior of Partial Monolayer Catalysts

The catalytic properties of materials containing less than a monolayer of  $V_2O_5$  were

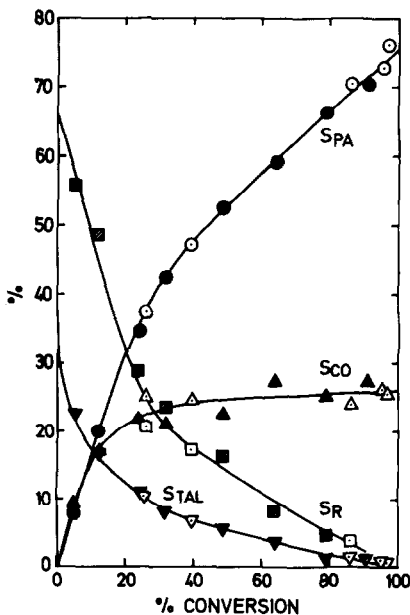


Fig. 13. Product selectivities at 582 K as a function of conversion. Open points,  $P_X$  variation; hatched points,  $P_O$  variation. The values are taken from Fig. 8A and 10, but not all points are shown for clarity.

investigated as outlined under Experimental between about 525 and 665 K using the standard reactant mixture: the uncoated support was also examined. This catalyzed the conversion of *o*-xylene principally to carbon oxides and carbonaceous residue ( $S_R = 42\%$ ,  $S_{CO} = 46\%$  at 20% conversion); tolualdehyde was the chief selective oxidation product ( $S_{TAL} = 13\%$  at 20% conversion; 30% at 5% conversion), with traces of phthalic anhydride ( $S_{PA} \approx 1\%$ ) at 620–650 K. The activation energy based on *o*-xylene removal was  $30.5 \text{ kJ mol}^{-1}$ . Aspects of the results obtained with the partial monolayer catalysts are shown in Fig. 14. There were complex differences in the changes of product selectivities with temperature which do not merit description or interpretation, but the most important feature was a progres-

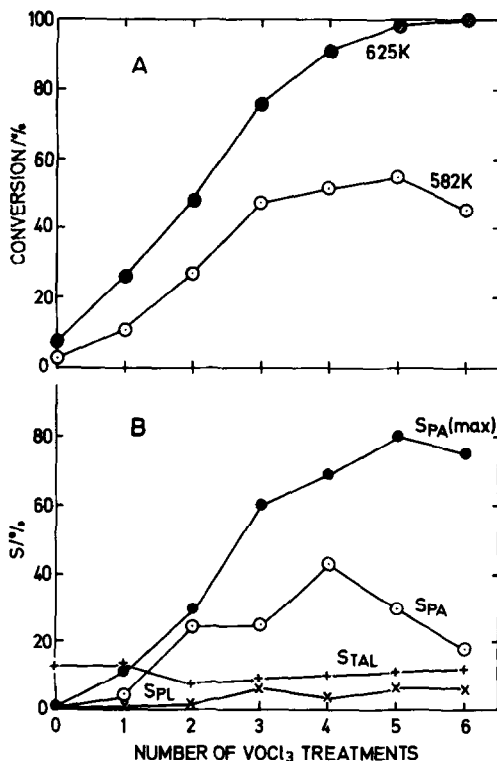


Fig. 14. Dependence upon number of  $VOCl_3$  treatments of (A) conversion at 582 and 625 K, and (B) product selectivities at 20% conversion, and maximum selectivity to phthalic anhydride. Symbols as in Figs. 1 and 2.

sive increase in both conversion and maximum phthalic anhydride yield with the number of treatments up to the fifth. The performance of the final catalyst, with which most of the foregoing results were obtained was slightly worse than that of its predecessor. The changes in product selectivities at 20% conversion are also shown in Fig. 14. One noteworthy feature is that with the first three catalysts (including the support) the maximum value of  $S_{PA}$  is almost achieved at 20% conversion. These catalysts therefore seem to be poor because they allow the further oxidation of *o*-xylene to nonselective products, rather than because of their inability to form it.

## DISCUSSION

### *The Fate of the Missing Carbon*

An important feature of the work described above is the discovery that below about 610 K a substantial part of the carbon fed to the catalyst as *o*-xylene is not recoverable as products detected by glc or ir analysis. The fraction of reacted *o*-xylene not recovered is denoted by  $S_R$ . It appears that there may be two processes which can account for the missing carbon: (i) the formation of a carbonaceous surface deposit and (ii) the formation of low volatility polymers. The evidence for this hypothesis is as follows.

We have been able to measure by oxidation the amount of carbon retained by the catalyst after a period of steady-state reaction (see Fig. 6). Of course we do not know what adsorbed species gives rise to the observed carbon dioxide, but the rapid disappearance of selective oxidation products on stopping the *o*-xylene flow suggests that it is not one which leads to desired products. It may for example be a dehydrogenated and strongly adsorbed form of the *o*-xylene molecule, or such a species may be the precursor to a carbonaceous deposit: this possibility will be considered further below. We believe it to be responsible for the initial loss in activity (see Fig. 3) although its ac-

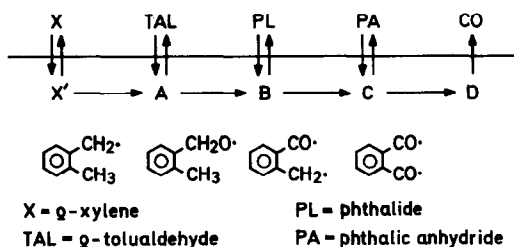
cumulation on the surface does not significantly affect the course of the reaction. Below about 560 K this strongly held species or deposit appears to monopolize the surface in the steady state (see Fig. 7), and the rate of the selective reaction is probably limited by the fraction of uncovered surface. In this region  $S_{CO}$  rises quickly, due perhaps to the competitive oxidation of the precursor, and the activation energy (76.5 kJ mol<sup>-1</sup>) may relate to this process. Between 525 and 610 K, the activation energy for the formation of the deposit is less than that for the process inhibiting its formation, so that the fraction of the surface which it occupies decreases progressively, especially above 560 K. At this temperature  $S_{CO}$  passes through a maximum (Fig. 2) and decreases up to 605 K in parallel with the decrease in the extent of the deposit coverage. This, combined with the information in Fig. 6 on the decrease in carbon oxides formation immediately upon stopping the *o*-xylene feed, strongly suggests that *below about 610 K the predominant source of the carbon oxides is oxidation of the deposit or its precursor*. The further increase in  $S_{CO}$  above about 610 K is due to the deep oxidation of phthalic anhydride. A change in the activation energy for *o*-xylene conversion, betokening a change in rate-determining step, occurs at 545 K (Fig. 1) which is close to the temperature at which the surface coverage by the deposit starts to decrease.

There are two other points concerning this surface deposit which deserve comment. First, during the transient changes at the higher temperatures (588 and 614 K),  $S_R$  decreased to a low limiting value or to zero (Fig. 3): this initial loss of carbon may be attributable to a small concentration of especially active sites. Second, at 582 K  $S_R$  increases with *o*-xylene pressure and decreases with increasing oxygen pressure (Figs. 8 and 10), while the same trends are observed even at 610 K (Figs. 8 and 11) where with the standard reactant ratio  $S_R$  is close to zero. We shall pursue the mechanistic implications below.

There is however evidence to show that not all of the missing carbon can remain on the surface. First there is the observation that it occurs in the steady state of reaction without causing a progressive loss of activity. Furthermore, below 560 K (Fig. 2) more carbon is lost than is recovered as carbon oxides. We believe that especially in this range of temperature the strongly adsorbed species desorb as a polymer of low volatility, thus providing a means of maintaining an equilibrium surface coverage. We have observed a condensate in the cooler parts of the system and indeed with other catalysts not covered in this report such products are formed in abundance and have even necessitated cleaning the sample valve and replacement of the chromatographic column. Tar has also been reported as a product of the ammoxidation of 3-picoline using unsupported  $V_2O_5$  as catalyst (23).

### Reaction Mechanisms

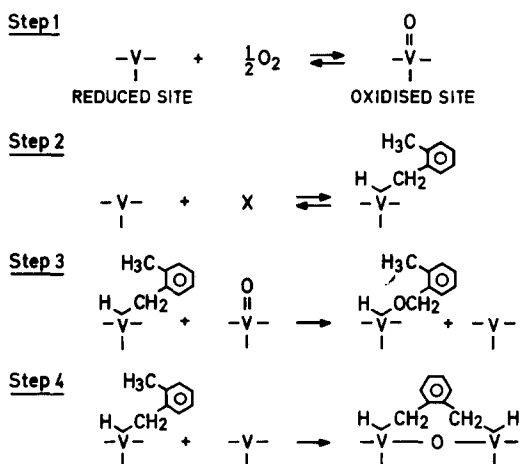
There are a number of discussions in the literature of the mechanism of the  $V_2O_5$ -catalyzed oxidation of *o*-xylene to phthalic anhydride (6, 7, 17), but these are generally couched in terms of likely reaction paths by which intermediates are converted into final products: no attempt has been made to describe the surface transformations in atomistic terms. It seems likely that there will be a sequence of adsorbed species, each convertible into the next by oxidation and from each of which one of the observable intermediates may be formed reversibly by desorption or some other simple reaction. Scheme I shows one possibility: it ignores



trace intermediates not quantified in this

work, and also the possibility that species A, B, and C may transform to others not shown, from which carbon oxides may be formed. We do not propose to speculate in detail about the structures of these adsorbed species, although we give illustrative examples of possible structures in the scheme: nor shall we speculate on the mechanisms of their interconversion. We concentrate now on the origin of the process by which carbon seems to disappear from the system.

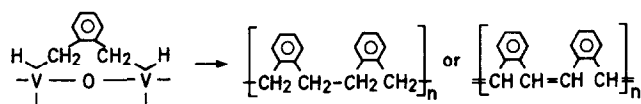
We start by following received wisdom (24) and describing the oxidizing species as an oxygen atom double bonded to a  $V^{5+}$  ion. This we describe as an *oxidized site*, and removal of the oxygen atom by desorption or by oxidation of an adsorbed species lead to a *reduced site* which can be reconverted to an oxidized one by the chemisorption of oxygen (Scheme II, step 1). We postulate that *o*-xylene adsorbs in the form denoted as X' in Scheme I by dissociative chemisorption at a reduced site (Scheme II,



step 2): this type of process is well known to occur with cations of Group VIII elements in lower oxidation states. This then transforms either by oxygen atom insertion or by addition of the dissociated *o*-xylene molecule across the  $V=O$  bond into species A (step 3) from which *o*-tolualdehyde is generated by dissociation of a hydrogen

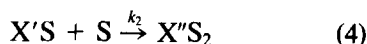
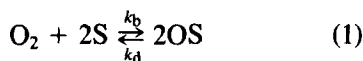
atom. We think that this first oxidation is the most crucial and difficult step in the entire reaction sequence, and that if successfully achieved the further transformation of A successively into B, C and then phthalic anhydride follows quickly and without major difficulty. The principal risk is that the X' form of adsorbed *o*-xylene may convert to another from which selectively oxidized products may not be formed. We note that carbon loss is suppressed by increasing oxygen pressure (see Figs. 10 and 11). It is

therefore reasonable to postulate that X' transforms to a second species X'' by reaction of the other methyl group with another reduced site leading to the strongly adsorbed species depicted in step 4 of Scheme II. This may well be the species whose initial formation at temperatures below about 600 K results in loss of activity (see Figs. 3 and 5) and which is only removable by non-selective oxidation (Fig. 6): alternatively, it may polymerize and/or dehydrogenate, as shown in Scheme III. The substances



which have been observed to condense in the cooler parts of the system may be low-molecular-weight polymers of this kind.

If these presumptions are correct, the kinetics and product selectivities are largely determined by the events which occur at the beginning of the reaction sequence and which may be formulated as follows, X representing gaseous *o*-xylene, S a reduced site, OS an oxidized site, and A the species A in Scheme I.



This reaction set reproduces qualitatively the principal features of the results. If step 3 is rate-controlling for the formation of selective products, its rate depends upon  $\theta_{X'}$  (the surface coverage by X'), which will increase with increasing  $P_X$  (Fig. 9), and upon  $\theta_O$  (the surface coverage by oxygen atoms) which will likewise increase with increasing  $P_O$  (Figs. 10 and 11). The rate of formation

of the strongly adsorbed species X'' depends upon  $\theta_{X'}$  (Fig. 9) but not upon  $\theta_O$  (observed orders in  $P_O$ , zero to 0.2). If X'' is the principal source of carbon oxides at all temperatures, the rate of their formation will depend in turn upon  $\theta_{X'}$ , and hence upon  $P_X$ , and upon the oxygen atom concentration (Fig. 12).

Unfortunately the conventional steady-state analysis of this apparently simple scheme has proved extraordinarily difficult, even with the simplifying assumptions that the surface coverage by A is low (due to its rapid further oxidation) and that coverage by X'' is also low (by reason of its desorption as the volatile polymer). Elimination of step 4 transforms the problem, as does the assumption that  $\theta_{X'}$  is small and hence that step 3 does not materially affect the oxygen adsorption-desorption equilibrium. In this case  $\theta_O$  is proportional to  $P_O^{1/2}$  (providing  $k_d \gg k_b$  and  $\theta_{X'}$  is proportional to  $P_X$  (provided  $\theta_{X'}$  is small). On this basis the rate of formation of selective products derived from A equals  $k_1 P_O^{1/2} P_X$  (which is approximately what is found) and for polymeric products derived from X'' the rate equals  $k P_O^0 P_X$  (which again approximates to the observations).

The foregoing reaction scheme differs in

some important respects from the classical Mars–van Krevelen scheme (15) which even in its most recent formulation (25) ignores the possibilities of chemisorption of the reactant hydrocarbon and of the reaction between chemisorbed hydrocarbon and atomic or lattice oxygen being rate-determining. Shelstad *et al.* (26) have considered this point and concluded that such a step would be kinetically indistinguishable from a sequence of steps involving alternate reduction and reoxidation of the surface. This is so provided that chemisorbed oxygen is an intermediate in reoxidation and that the two component rates are comparable in magnitude. Our own results indicate that the reaction of chemisorbed *o*-xylene with chemisorbed oxygen (step 3) is slower than the rates of chemisorption of either reactant (steps 1 and 2).

In conclusion, we believe that below about 560 K the rate of reaction is limited by the amount of surface not covered by strongly adsorbed species derived from the dissociative chemisorption of *o*-xylene, and that under the conditions of measurement of the kinetics, where much or all of the surface is free of such species, the surface coverage by both *o*-xylene (as X') and of oxygen atoms is rather low. In this way we can give a reasonable explanation of most of the observations.

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