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The Catalytic Vapor-Phase Oxidation of o-Tolualdehyde

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A study was made of the oxidation of *o*-tolualdehyde over fused vanadium oxide from 360° to 460° in a flow system.

The reaction course consists of four parallel routes: (1) the stepwise oxidation of *o*-tolualdehyde to phthalic anhydride via *o*-toluic acid and phthalide intermediates; (2) the direct oxidation to phthalic anhydride; (3) the formation of carbon oxides from intermediate maleic anhydride; and (4) the direct oxidation to carbon oxides.

The activation energy for the over-all reaction (disappearance) of *o*-tolualdehyde is 24.7 kcal/mole in the range 370° to 415° and the reaction order is 0.97 with respect to the concentration of *o*-tolualdehyde. The rate of oxidation shows a square root dependence on the oxygen concentration below 0.2 atm. The Hinshelwood treatment suggests that steady state conditions are established on the catalyst surface.

INTRODUCTION

A study of the vanadia-catalyzed vapor-phase oxidation of *o*-methylbenzyl alcohol (*1*), which was recently carried out in this laboratory, showed that *o*-tolualdehyde was the main intermediate in the stepwise oxidation process leading to phthalic anhydride. Other authors (*2*, *3*, *4*) also reported that in the oxidation of *o*-xylene in the presence of the same catalyst, *o*-tolualdehyde was an intermediate under given conditions. However, the role of *o*-tolualdehyde as a branch-forming intermediate in the oxidations of *o*-xylene and *o*-methylbenzyl alcohol has not been clarified. It was found in the course of our work that increased formation of carbon oxides from *o*-methylbenzyl alcohol, and from *o*-xylene, occurred under conditions at which *o*-tolualdehyde was formed in highest concentrations. This result may tentatively be explained by competitive degradation reactions of *o*-tolualdehyde which would lead by way of toluene and benzoic acid eventually to carbon oxides. There was reason to believe that the degradation reactions probably take place with lower activation energies than the sequential process and become less significant at the higher temperatures.

Finally, it is noted that data on the reaction kinetics of the catalytic oxidation of *o*-xylene are few (*2*, *4*, *5*), with no firm agreement on the reaction mechanism involved. Kinetic data on the vanadia-catalyzed oxidation of *o*-tolualdehyde are completely lacking.

A basic study of the vanadia-catalyzed oxidation of *o*-tolualdehyde was therefore of interest both for clarifying the mechanism of the *o*-xylene oxidation and for a better understanding of the oxidation processes which take place on the catalyst surface.

EXPERIMENTAL

The apparatus, the method of analysis, and the experimental procedure used in this work, apart from some details, were described in a previous communication (*1*). Six reactors of identical annular design but different lengths were used. Their volumes were 0.8, 1.6, 2.1, 3.0, 4.4, and 8.3 ml. The reactor was filled with granules of fused vanadium pentoxide (Vanadium Corporation of America, CP grade, 99.9% pure) and immersed in an electrically heated and stirred salt bath controlled to ±0.5°. The catalyst had a surface of 2 m^2 (*6*). The void volume of the catalyst bed, determined as the volume of water which could be contained within a measured volume of catalyst,

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was 0.6 ml/ml of catalyst bed. The average increase of temperature in the catalyst bed above that in the salt bath was about 1°. The concentrations of *o*-tolualdehyde in the gas mixture entering the reactor were 0.62, 0.75, 0.93, 1.24, and 1.86 $\times 10^{-4}$ mole/liter, respectively. This corresponds to oxygen to aldehyde mole ratios of 150, 125, 100, 75, and 50 to 1. The contact times varied from 0.15 to 0.6 sec and were calculated from the void space of the catalyst bed and the feed rate of the reaction mixture corrected to the temperature and pressure in the reaction chamber. The mass velocity was 18 to 56 $\times$ 10^{-4} g cm^{-2} sec^{-1}.

In order to determine the mass transfer effect on the product distribution, experiments were carried out in a specially designed reactor at a mass velocity of 473 $\times$ 10^{-4} g cm^{-2} sec^{-1} but otherwise unchanged conditions. Since results were identical to those at lower mass velocities, it was concluded that mass transfer effects due to the geometry of the reactor were not significant.

MATERIALS

o-Tolualdehyde was prepared (*7*) by oxidizing *o*-xylene (Phyllips 99.97% pure) with chromium oxychloride in a chloroform solution between 0° and 10°. The addition complex formed was decomposed by adding the slurry portionwise with cooling to an aqueous solution of sodium sulfite followed by steam distillation. The *o*-tolualdehyde obtained in this manner was 94% pure. The product was then purified by forming the sodium bisulfite compound followed by decomposition of the adduct in the conventional manner. Upon fractionation of the yellow oil at a pressure of 10 mm and 90.5°, 99.8% pure *o*-tolualdehyde was obtained, b.p. 199° at 758 mm Hg, n_D^{20} 1.5477; 4-nitrophenylhydrazone from 95% ethanol, m.p. 221°. The purity of the *o*-tolualdehyde was also established both by high-temperature mass spectrometry and gas-liquid chromatography. *o*-Tolualdehyde was found to be very susceptible to autoxidation even at temperatures below 10°. Upon exposure to air at room temperature *o*-tolualdehyde peroxide, per-*o*-toluic acid, and *o*-toluic acid began to form in a few hours.

TABLE 1

PRODUCT DISTRIBUTION IN THE GAS-PHASE OXIDATION OF *o*-TOLUALDEHYDE

Concentration: 1.24 $\times 10^{-4}$ mole *o*-tolualdehyde/liter
9.30 $\times 10^{-3}$ mole oxygen/liter
Temperature: 450°
Contact time: 0.6 sec

	Homogeneous (mole %)	Catalytic (mole %)
o-Tolualdehyde	96.1	3.5
o-Toluic Acid	1.8	0.5
Per-*o*-Toluic Acid[a]	1.7	0.2
Phthalide	0.1	2.9
Maleic anhydride	0.1	3.4
Carbon oxides	0.1	12.7
o-Formylbenzyl alcohol	Trace	Trace
o-Methylbenzyl alcohol	Trace	—
o-Xylene	Trace	0.1
Phthalic anhydride	—	76.6
	99.9	99.9

[a] *o*-Tolualdehyde peroxide and hydroperoxides obtained by oxidation of the nucleus are present in very small concentrations.

RESULTS

In Table 1, product distributions are shown for both the homogeneous (noncatalytic), and catalytic oxidations of *o*-tolualdehyde under the same experimental conditions. In the homogeneous oxidation 96.1 mole % of *o*-tolualdehyde was recovered unchanged. The remainder consisted principally of *o*-toluic acid and per-*o*-toluic acid. In the catalytic reaction the main product was phthalic anhydride. Since the contribution of the homogeneous reactions in the catalytic process was very small, the measured catalytic rates were used without correction for this effect.

In Figs. 1 and 2, data for the formation of individual products are plotted as a function of temperature for each of the five initial concentrations of *o*-tolualdehyde at a contact time of 0.6 sec. The type of products formed depends on the temperature, and the rate of formation varies with the initial concentration of *o*-tolualdehyde.

Below 390° *o*-toluic acid is the main product. Above 390° the formation of phthalic anhydride rapidly increases and passes through a maximum between 425° and 435°, depending on the composition of the gas mixture used. The formation of

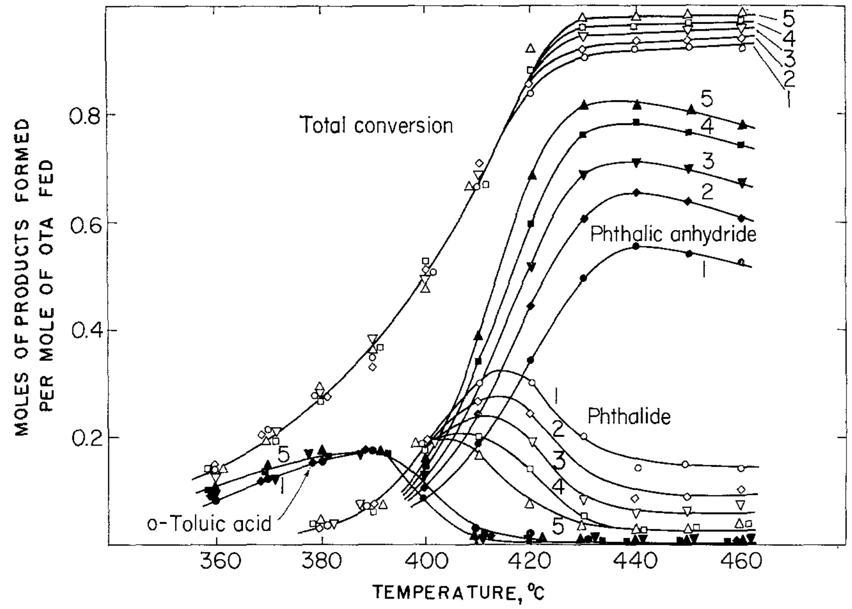


FIG. 1. The oxidation of *o*-tolualdehyde (OTA) over vanadia catalyst. Average oxygen concentration, 9.30 × 10^{-3} mole/liter. Contact time, 0.6 sec. Initial OTA concentrations: (1) 0.62; (2) 0.75; (3) 0.93; (4) 1.24; (5) 1.86 × 10^{-4} mole/liter.

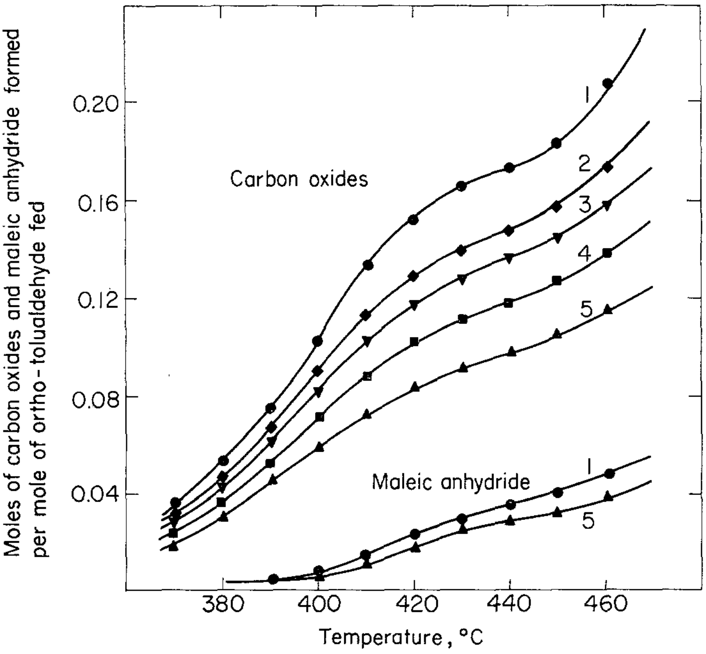


FIG. 2. The formation of maleic anhydride and carbon oxides, respectively, from *o*-tolualdehyde (OTA) over vanadia catalyst. Average oxygen concentration, 9.30 × 10^{-3} mole/liter. Contact time, 0.6 sec. The initial OTA concentrations: (1) 0.62; (2) 0.75; (3) 0.93; (4) 1.24; (5) 1.86 × 10^{-4} mole/liter. The concentration of carbon oxides is expressed as moles of *o*-tolualdehyde required for the formation of carbon oxides per mole of *o*-tolualdehyde employed. In these values account was taken for the amount of carbon oxides formed concurrently with maleic anhydride.

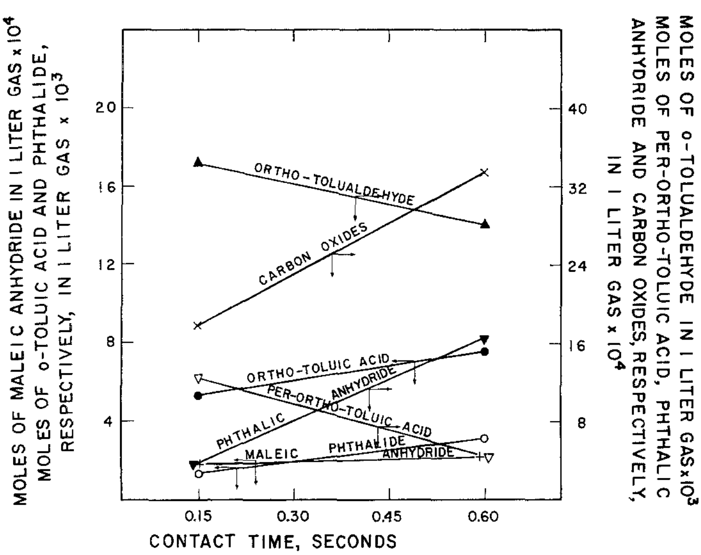


FIG. 3. Variation with contact time of the concentration of *o*-tolualdehyde, *o*-toluic acid, per-*o*-toluic acid, phthalide, maleic anhydride, phthalic anhydride, and carbon oxides in the gas leaving the catalyst bed. In the values for carbon oxides account was taken for the amount formed concurrently with maleic anhydride. Initial OTA concentration, 0.62×10^{-4} mole/liter. Oxygen concentration, 9.30×10^{-3} mole/liter. Temperature, 390°.

phthalide exhibits similar behavior with rising temperature, and shows a maximum between 405° and 415°.

The formation of carbon oxides and maleic anhydride passes through an inflection at a temperature of 430° which corresponds to that of the maximum formation of phthalic anhydride. At temperatures higher than 430° the concentration of these products increases primarily as a result of the oxidation of phthalic anhydride. It appears that both phthalide and *o*-tolualdehyde undergo destructive oxidation to a lesser extent than phthalic anhydride under these conditions, probably due to their lower concentrations.

Two possible routes for the formation of phthalic anhydride are considered here:

(1) Phthalic anhydride is formed by a consecutive series of reactions in which *o*-toluic acid and phthalide are intermediates.

(2) Phthalic anhydride is formed by a process parallel to (1) directly from *o*-tolualdehyde.

With regard to these points, two series of experiments at 390° and 430° were carried out in which the contact time was varied while the concentrations of reactants were kept constant. At 390° (Fig. 3) the concentration of *o*-toluic acid increased at longer contact times while a decrease occurred in the concentrations of *o*-tolualdehyde and per-*o*-toluic acid. This indicates that a reaction leading to *o*-toluic acid from *o*-tolualdehyde via per-*o*-toluic acid is involved. Furthermore, if phthalide is an intermediate in the formation of phthalic anhydride under these conditions, the mole ratio of phthalic anhydride to phthalide formed should increase with an increase in contact time. If phthalic anhydride is formed directly from *o*-tolualdehyde (or *o*-toluic acid), this ratio should remain constant unless the two reactions are of different order. A great difference in orders is not likely since the order of disappearance of *o*-tolualdehyde and the orders of formation of phthalide and phthalic anhydride were found to be 0.97, 0.99, and 0.84, respectively.

At 390°, an increase was observed in the mole ratio of phthalic anhydride to phthalide from 0.27 to 0.53 as a result of an increase in contact times from 0.15 to 0.6 sec (Table 2). At 430°, however, this ratio remains fairly constant. The mole ratios of phthalide to *o*-toluic acid and phthalic anhydride to

TABLE 2

Variation with Contact Time of the Mole Ratio of Compounds in the Gas Leaving the Catalyst Bed at 390° and 430°

Initial gas composition at 390°: 0.62×10^{-4} mole of *o*-tolualdehyde/liter
9.30×10^{-3} mole of oxygen/liter
at 430°: 0.93×10^{-4} mole of *o*-tolualdehyde/liter
9.30×10^{-3} mole of oxygen/liter

Ratio (mole/mole)	Temperature:	390°		430°	
	Contact time (sec):	0.15	0.60	0.15	0.60
Phthalic Anhydride to Phthalide		0.27	0.53	8.1	8.0
Phthalide to *o*-Toluic Acid		0.25	0.41	17.9	17.2
Phthalic Anhydride to *o*-Toluic Acid		0.07	0.22	144.5	138.0
Carbon Oxides to Maleic Anhydride		10.0	15.0	4.7	4.7

o-toluic acid exhibit similar behavior with rising contact time but otherwise unchanged conditions.

The fact that no toluene or benzoic acid were found among the oxidation products ruled out the possibility that competitive degradation reactions occurred, especially at lower temperatures where *o*-tolualdehyde was present in the highest concentration. One may assume that these reactions, representing an alternate interpretation of the data, probably take place with lower activation energies than the sequential process and become substantially less significant at the higher temperatures. The degradation reactions of *o*-tolualdehyde, probably occurring by way of a free radical mechanism, were found to become significant at contact times higher than 8 sec under otherwise comparable conditions.

It was therefore concluded that at lower temperatures and partial conversions of *o*-tolualdehyde the phthalic anhydride is formed at least in part from *o*-tolualdehyde by a consecutive series of reactions in which *o*-toluic acid and phthalide are intermediates. At higher temperatures such as 430° the direct oxidation of *o*-tolualdehyde to phthalic anhydride predominates.

Concerning the formation of carbon oxides and maleic anhydride two alternatives were considered:

(1) Carbon oxides are formed by a stepwise process in which maleic anhydride is an intermediate.

(2) Carbon oxides and maleic anhydride are formed by two simultaneous reactions.

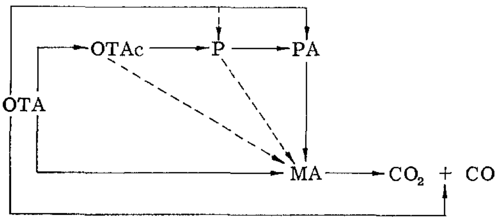
With regard to these points the mole ratios of carbon oxides to maleic anhydride in the oxidation product were determined at two different contact times at 390° and 430°, respectively (Table 2). The reaction order of the formation of carbon oxides from *o*-tolualdehyde was found to be 0.51 under these conditions. An increase of the mole ratio from 10 to 15 by an increase in contact time from 0.15 to 0.6 sec was observed at 390° (Table 2). At 430°, however, this ratio remained unchanged.

It was concluded that at lower temperatures and partial conversions of *o*-tolualdehyde, the carbon oxides are formed from *o*-tolualdehyde by a sequential process in which maleic anhydride is the intermediate. At higher temperatures such as 430° the direct oxidation to carbon oxides appears to become competitive with the postulated stepwise route. A portion of both carbon oxides and maleic anhydride is also probably formed from the precursors of phthalic anhydride.

The data in Figs. 1 and 3 and Table 2 therefore appear to be consistent and can be represented with the reaction scheme at the top of p. 130.

The mole ratio CO/CO_2 (0.068 at 390° and 0.149 at 460°) in the effluent gas increased about 4.2 times as the concentration of *o*-tolualdehyde was increased from 0.6 to 1.8×10^{-4} mole/liter. The ratio increased 2.2 times as the temperature was changed from 390° to 460°, at otherwise unchanged conditions.

In Fig. 4 the over-all reaction rate (disappearance) of *o*-tolualdehyde is plotted as a function of the average of initial concen-



OTA - *o*-Tolualdehyde
OTAc - *o*-Toluic acid
P - Phthalide
PA - Phthalic anhydride
MA - Maleic anhydride

—— Well-established route
---- Probable route

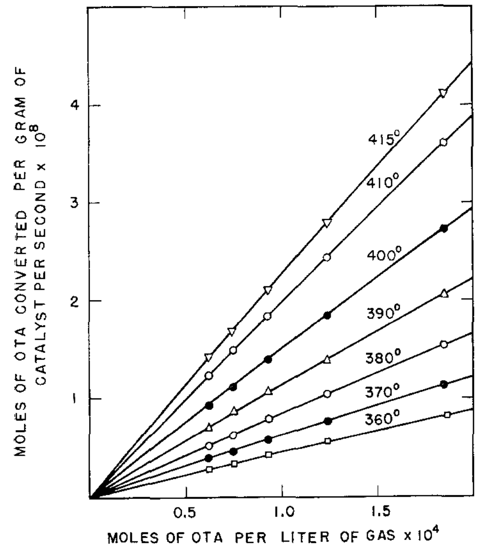


FIG. 4. Rate of oxidation of *o*-tolualdehyde (OTA) as a function of the initial concentration of OTA. Average oxygen concentration 9.30 × 10^{-3} mole/liter.

tration of *o*-tolualdehyde in the carrier gas. A series of rate isotherms is thus obtained. The apparent order of reaction, amounting to 0.97, was determined from the slopes of the lines in a plot in which logarithms of the reaction rates were plotted against the logarithms of the initial concentrations of *o*-tolualdehyde in the gas mixture. The variation of the k_1 values with the initial concentration of *o*-tolualdehyde calculated by using this reaction order at four different temperatures is given in Table 3. The logarithms of the averaged specific rate constants show a linear relationship to reciprocal temperature (Fig. 5) and may be represented by the expression

$$\ln k_1 = 9.46 - (24750/RT) \qquad (1)$$

The activation energy for the over-all conversion of *o*-tolualdehyde in the temperature range studied is 24.8 kcal/mole.

The dependence of the over-all reaction rate on the oxygen concentration was determined at constant initial concentration of *o*-tolualdehyde, contact time, and temperature (Fig. 6). The rate changes proportionally with the square root of the oxygen concentration.

The rate data were also treated by the equation proposed by Hinshelwood (*8*)

$$r = k_r k_a C_r C_o / (k_a C_o + N k_r C_r) \qquad (2)$$

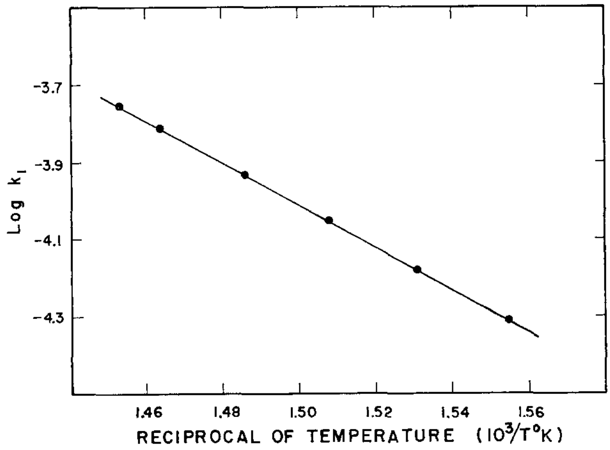


FIG. 5. Arrhenius plot of the over-all conversion (disappearance) of *o*-tolualdehyde from 370° to 415°.

TABLE 3

VARIATION OF THE OVER-ALL SPECIFIC RATE CONSTANT k_1 WITH THE INITIAL CONCENTRATION OF *o*-TOLUALDEHYDE IN THE GAS MIXTURE AT VARIOUS TEMPERATURES

$C \times 10^5$ (mole/liter)	$k_1 \times 10^7$ (liter g^{-1} sec^{-1})			
	380°	390°	400°	410°
6	6.5	9.0	11.7	15.4
8	6.6	8.8	11.7	15.4
10	6.6	9.0	11.8	15.4
12	6.7	8.9	11.8	15.4
14	6.6	8.9	11.7	15.4
16	6.6	8.8	11.7	15.4
18	6.6	8.8	11.7	15.4
Av.	6.6	8.9	11.7	15.4

for surface reactions in which the specific rate of adsorption of oxygen r_a and the specific rate of chemical reaction r are of the same order of magnitude under steady state conditions; k_r is the specific rate constant of reaction of organic reactant; k_a the specific rate constant of adsorption of oxygen; C_r and C_o the concentrations of organic reactant and oxygen, respectively, in the carrier gas; and N the mole ratio of oxygen consumed to *o*-tolualdehyde converted. It is supposed that only oxygen is chemisorbed on the catalyst surface; all the processes are first order in the concentration of each reactant, and the rate of desorption of oxygen is negligible. According to this interpretation the rate constant k_a should be independent of the organic compound employed if the same catalyst is used. The general treatment and the method of application were described in detail in a previous communication (*9*). The results are listed in Table 4. The Arrhenius temperature coefficient of k_a is 27.1 and that of k_r, 25.1 kcal/mole. The k_a values determined from a modified Hinshelwood expression in which the dissociative adsorption of oxygen is taken into account as demanded by the result in Fig. 6 [$K_1 = N/k_aC_o^{1/2}$ in Eq. (5) of ref. 9], were found to be about 1/10 of those listed in Table 4. The activation energies, however, remained unchanged.

TABLE 4

CONSTANTS OF EQ. (2)

Average C_o = 9.3 × 10^{-3} mole/liter
Average N = 2.34

Temp. (°C)	$k_a \times 10^5$ (liter g^{-1} sec^{-1})	$k_r \times 10^5$ (liter g^{-1} sec^{-1})
370	6.25	6.47
380	8.16	8.78
390	11.24	11.68
400	16.02	15.48
410	20.21	20.32
415	24.35	23.14

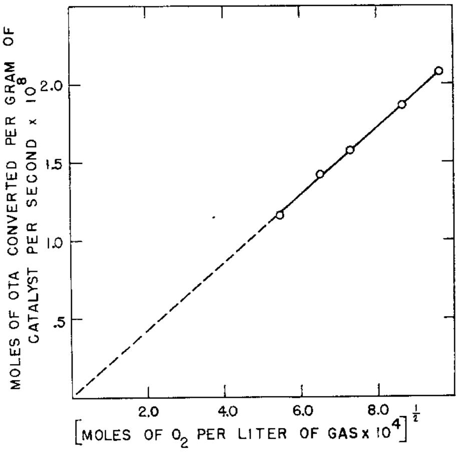


FIG. 6. Rate of oxidation of *o*-tolualdehyde (OTA) as a function of the square root of the initial concentration of oxygen in the carrier gas. Average OTA concentration, 1.86 × 10^{-4} mole/liter. Contact time, 0.6 sec and 390°.

To elucidate the role of the lattice oxygen of the vanadium oxide in the oxidation process, a gas mixture of 0.4 mole % *o*-tolualdehyde in prepurified nitrogen was passed over V_2O_5 at 420° and 0.6-sec contact time. Under these conditions when the direct oxidation mechanism was postulated, normal yields of phthalic anhydride were observed only in the first minutes of the experiment. After 10 min the carbon oxides increased to 40 mole % of the aldehyde (Fig. 7), passed through a maximum of 69 mole % after 50 min, and gradually decreased to 9 mole % after 6 hr. At this point the catalyst was almost completely reduced to V_2O_4 (confirmed by X-ray), and only *o*-tolualdehyde

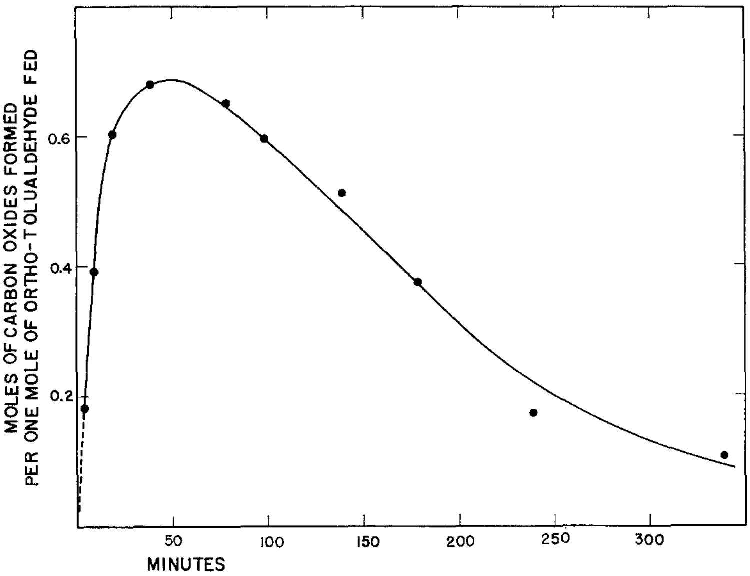


FIG. 7. Formation of carbon oxides from *o*-tolualdehyde (OTA) over vanadia as a function of time when no oxygen was present in the gas mixture entering the reactor. Concentration of OTA is 0.4 mole % in prepurified nitrogen. Temperature, 420° and contact time, 0.6 sec. The concentration of carbon oxides is expressed in moles of OTA required for the formation of carbon oxides per mole of OTA employed. No account was taken for the carbon oxides formed concurrently with maleic anhydride.

was recovered. Since the feed rate of *o*-tolualdehyde was 95 mg/hr and the mole ratio of oxygen consumed to *o*-tolualdehyde converted was 2.34, as determined from the product distribution in the oxidation run, the rate of oxygen uptake was 3.76×10^{19} oxygen molecules/min. This uptake can be related to the number of oxygen sites in the catalyst bed. If the oxygen ions in the lattice are all 3.0 Å apart (*10*), then about 8.9×10^{19} oxygen sites existed in the 8-m^2 surface area of the 4 g (2 m^2/g) of vanadium oxide. This suggests that in the initial period of 4 min of the reaction only 1.5 to 2 surface layers of oxygen of the catalyst participated in the reaction.

DISCUSSION

As shown in Fig. 4, the *o*-tolualdehyde disappearance rate tends to become less concentration-dependent at lower temperatures and higher concentrations. Throughout, the order of reaction is 0.97. The explanation for these results is that *o*-tolualdehyde undergoes oxidation mainly in the adsorbed state, and its rate of adsorption controls under certain conditions the overall rate of oxidation. In this case the Hinshelwood steady state approach applies only if the *o*-tolualdehyde adsorption rate $r_{a'}$ and the reaction rate r are also of the same order of magnitude. This modification, inherent to the steady state concept outlined above, is permissible.

The rate of *o*-tolualdehyde consumption is 0.5 order in oxygen and the specific rate constant for the adsorption of oxygen (3.1×10^{-5} liter g^{-1} sec^{-1} at 350°, determined by extrapolation from data in Table 4) agrees within an order of magnitude with those reported in the literature for the oxidation of other compounds (*9, 11, 12, 13*). This suggests that the adsorption of oxygen is dissociative and that steady state conditions as defined by Hinshelwood are established on the catalyst surface. In this case $r_a \leqq r \geqq r_{a'}$. It was found that $k_a < k_{a'}$ (*9*). However, in the steady state situation r_a must be greater than $r_{a'}$. This explains why a large excess of oxygen is always required during the oxidation process in order to keep the catalyst from being reduced.

The temperature coefficients of k_l, k_r, and k_a (24.8, 25.1, and 27.1 kcal/mole, respectively) agree satisfactorily with the 28 kcal/mole activation energy (*14*) required for oxygen to reach the transition state. The addition of oxygen may therefore involve electronically excited, adsorbed molecular oxygen.

The presence of per-*o*-toluic acid in the oxidation product indicates that the formation of *o*-toluic acid may occur in part by way of free radicals. The formation of perbenzoic acid and hydroperoxides from toluene was proposed by Pichler and Obenaus (*15*). However, they did not isolate the compounds. Oxygen atoms (*16*) and free radicals (*2, 17*) were shown to be of little importance in the catalytic oxidation of benzene and xylene. There is, however, ample evidence for the existence of ionic species of xylene (*2*), naphthalene (*18*), and olefins such as ethylene and propylene (*19, 20*) on the surface of oxidation catalysts. Stable paramagnetic surface species derived from naphthalene and anthracene were also observed on vanadium oxide (*21*). Therefore, it appears reasonable to assume that in the *o*-tolualdehyde oxidation the major portion of aldehyde surface species are either positive ions or activated complexes.

Data in Table 2 show that the sequential oxidation reactions occur at milder conditions whereas at more severe conditions the direct process becomes significant. Therefore, the chemisorption of the *o*-tolualdehyde on the catalyst surface can be visualized as taking place by either (1) the aromatic ring, or (2) the carbonyl group, or (3) the methyl group, or (4) both the carbonyl and methyl groups. The chemisorptions of types (1) and (2) occur at milder conditions whereas at more severe conditions chemisorption of type (4) becomes significant. If the positive center once formed remains localized at the part of the molecule adsorbed on the surface, then the oxygen attacks this part. Thus, with milder conditions, the carbonyl-adsorbed *o*-tolualdehyde should oxidize to *o*-toluic acid, whereas the nucleus-adsorbed molecule should oxidize to maleic anhydride and carbon oxides by way of ring rupture. This is in good agreement with the experiment. Single methyl group adsorption hardly occurs; only trace amounts of *o*-formylbenzyl alcohol and very small concentrations of phthalide (possibly from the dialdehyde by isomerization) were found among the products under these conditions (Fig. 1 and Table 1).

At more severe conditions adsorption by way of the methyl group of the *o*-tolualdehyde molecule, which is already chemisorbed by way of the carbonyl group, becomes significant. This adsorption may occur either simultaneously with that of the carbonyl group or subsequently, i.e., after the aldehyde has been oxidized to *o*-toluic acid. In either case a temporary decrease of the rate of formation of carbon oxides in favor of phthalic anhydride, as observed in Fig. 2, would be expected.

The role of vanadium oxide in the oxidation process is not clear. Some authors (*2, 22, 23*) claim that the catalyst is first reduced by supplying lattice oxygen to the adsorbed species and is then regenerated by atmospheric oxygen. Others propose that the reaction occurs with chemisorbed oxygen (*14, 24*). The active oxides are V_2O_5, $V_2O_{4.34}$, and intermediate structures (*25, 26*). The O–O distances in the $V_2O_{4.34}$ lattice, however, are essentially the same as those in V_2O_5 (*10, 23*). This can be explained either by the change in number of shared elementary cells with oxygen (*27*) or by only partial removal of oxygen from the lattice while the original V_2O_5 structure remains essentially unchanged.

It is proposed that a point-to-point congruence between the adsorbed molecule and the lattice oxygen of the catalyst is required in the direct process; whereas in the sequential process the adsorbed oxygen rather than the lattice oxygen participates in the reaction. The striking similarity between certain atomic distances in the *o*-tolualdehyde molecule and those in the V_2O_5 (or $V_2O_{4.34}$) support this assumption.

Thus, the C–C distance between the methyl and carbonyl groups in *o*-tolualdehyde (2.8 Å) and that between C_1–C_4 in benzene (2.79 Å) compare with the O–O distance in V_2O_5 (*27*) along the trigonal base (2.8 Å), whereas the C_1–C_3 distance in benzene (2.41 Å) agrees with the O–O distance of the two shorter bipyramid sides (2.39 Å).

A similar relationship exists in the oxidations of *o*-xylene, naphthalene, tetralin, and indene. According to the above interpretation any oxide from $V_2O_{4.34}$ to V_2O_5 should be and is, indeed, an active catalyst. In oxygen-lean mixtures the vanadium oxide catalyst is further reduced, thus producing a different catalyst (*25*) which is no longer suitable for a point-to-point adsorption. This new catalyst promotes abundant formation of carbon oxides (*1*, *23*, *28*), whereas V_2O_4 is catalytically inactive. This is in good agreement with experiment (Fig. 7). Finally, the interatomic distances in the oxygen molecule, ion O_2^-, and ion O_2^{2-} (1.21, 1.26, and 1.49 Å, respectively) suggest that in the direct oxidation process the reaction of *o*-tolualdehyde with these species, either adsorbed or in the gas phase, is not likely.

In the direct oxidation process only about 1.5 to 2 surface layers of catalyst lattice oxygen participate in the reaction. On the other hand, data on the isotope exchange of O_{18} with CO on oxidic catalysts (*19*) indicate that the catalyst lattice oxygen does not participate in low-temperature hydrocarbon oxidations.

The mechanism which emerges for the oxidation of *o*-tolualdehyde is that at milder conditions (stepwise process) the adsorbed aldehyde in the form of either an active surface species or an ion undergoes oxidation by oxygen ions loosely adsorbed on the surface. At more severe conditions (direct process) the reaction with lattice oxygen of a few top layers of the catalyst predominates.

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