The Influence of Electron Directing Effects on the Catalytic Oxidation of Toluenes and Xylenes

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The relationship between the catalytic activity of an oxidation system and the electron directing properties of hydrocarbons has been investigated using the oxidation of unsubstituted and substituted toluenes over molybdenum trioxide. This catalyst is found to be selective but rather inactive, with a maximum activity in the temperature range 450–460°C.

Kinetic studies of the oxidation of toluene show that the reaction is controlled by the rate of reduction of the catalyst. Comparison with the results for xylenes shows that the formation of the hydrocarbon–molybdenum complex is the slow step. The oxidation of substituted toluenes is found to be controlled by the rate of the surface reaction between adsorbed oxygen and toluene.

The electron directing properties of the organic fuel are found to be affected by substituents in the molecule and by the field effects of the catalyst. Catalytic activity is found to be proportional to these modified electron directing properties, and the system obeys a linear free energy relationship similar to the Hammett equation.

INTRODUCTION

Studies of catalytic oxidation have led to the conclusion that the formation of adsorbed intermediates is often associated with the transfer of an electron between the adsorbate and the catalyst (1). Changes in the electron work function of silver catalysts with adsorption of the components of ethylene oxidation (2) is a case in point. Indeed, the selectivity and activity of a given oxidation catalyst often depends upon the strength of chemical bonding, and hence on the possibility of electron transfer between the adsorbate and the catalyst (1). Particular attention has been focused on electron transfer from the catalyst to produce charged oxygen species (3), and catalytic activities have been related to the possibility and strength of oxygen bonding. For example, molybdenum trioxide has been suggested to be a selective (if not very active) catalyst because the only active chemisorbed oxygen entity appears to be O^{2-} (4): other diatomic species that are

known to exist on the catalyst (5) are not involved in the catalytic oxidation. Again, Moro-oka et al. (6) have shown that the catalytic activity of a series of metal oxides for the oxidation of isobutene, acetylene, ethylene, and propane can be correlated with the heat of formation of the metal–oxide bond. Similar relationships between strengths of adsorption and catalytic activities have been observed in oxidation (7) and in other systems (8).

The possibility of electron transfer from organic fuels to the catalyst has also been studied, although most interest has been paid to the possibility of removal of allylic hydrogens to form symmetrical, possibly π adsorbed, intermediates (9). Batist et al. (10–12) have suggested that this reaction, as it occurs during the oxidative dehydrogenation of butene-1 to butadiene over bismuth molybdate, involves the production of a charged allyl ion which bonds to a Mo^{6+} ion. Moro-oka and Ozaki (13) conclude that the adsorption of olefins onto nickel oxide involves a π complex and electron donation

to the solid. Little work has been done, however, to try and relate catalytic oxidative selectivity and activity with the electron donating characteristics of the organic fuels. In the present study, the oxidation of a series of substituted and unsubstituted toluenes was used to examine such relationships.

The ease of electron transfer to the catalyst from a hydrocarbon will depend primarily upon the density and localization of charge. This, in turn, may be controlled by the substitution of electron directing groups (such as methyl or chlorine) into the molecule (15): such substituents must not, however, become chemically involved in the reaction. The catalytic oxidation of the side chain of ring substituted toluenes offers a combination of geometric isolation and electrical conduction between the substituents and the site of attack. Studies have been concentrated on the oxidation of unsubstituted and methyl- or chloro-substituted toluenes over molybdenum trioxide. This catalyst, which allows adsorbed oxygen to act only as O^{2-}, has been characterized to some extent during studies of bismuth molybdate catalysts (10–12).

EXPERIMENTAL METHODS

Materials

AnalaR grade toluene and reagent grade chlorotoluenes were obtained from Hopkin and Williams, and purified by further distillation. Xylenes, obtained from B.D.H., were also purified by distillation. Substituted and unsubstituted aromatic aldehydes, benzoic acid, toluic acids, and organic anhydrides were obtained commercially and were used without further purification. Phthalan was prepared by the method described by Stephenson (14).

Oxygen and nitrogen from cylinders were purified by passage through beds packed with magnesium perchlorate and sofnolite. Carbon dioxide and argon were passed through a glass wool filter before use.

Sufficient catalyst was prepared so that the same material could be used for all experiments. Pumice stone (Hopkin and Williams) was ground, washed well with water, dried, and sieved. Particles of mesh size 10–14 were mixed with a 20% solution of ammonium molybdate (AnalaR) in distilled water and allowed to stand overnight. The excess solution was decanted, and the impregnated solid was dried and activated. This last process involved heating at 200°C in a current of air and slowly increasing the temperature to ca. 500°C (overnight). The catalyst was cooled, re-sieved, and stored in a desiccator.

Apparatus and Procedure

A standard flow apparatus has been used to measure reaction rate data. A measured stream of gas was passed through a bubbler maintained at a preset temperature (controlled to within ±0.1°C) which contained the hydrocarbon fuel, and then through a vessel fitted with glass sinters and maintained at the same temperature. Considerable difficulty was experienced in obtaining a constant and reproducible flow of fuel vapor with all toluene fuels. Various methods of near-saturation followed by cooling (17), coupled with alternative bubbler designs, were found to give irreproducible results, even though fuels such as benzene or hexene behaved as expected. It was eventually found necessary to use an extended series of bubblers packed with glass ballotini to obtain reproducible "pickup" amounts of fuel. The necessary gas–liquid contact time was estimated to be of the order of five times the predicted value. Suitable adjustments of the temperature of the bath and the gas flow rate, coupled with the control of secondary nitrogen and oxygen streams, allowed the production of a measured flow of gas containing any required concentration of fuel and oxygen. The composition and reproducibility of this feed could be estimated by trapping out the condensable fuel or by injecting a sample, via an on-line sampling valve, into a gas chromatograph.

The catalyst was supported in a tubular reactor placed in an electrically heated air oven. The temperature of the catalyst bed in the absence of reaction was controlled to within ±0.2°C by an A.E.1. R.T.3.R. proportional controller.

The products of reaction could be analyzed either directly in a gas chromatograph, or by trapping and subsequent analysis. No difference between the results from either method was observed and the trapping technique was preferred for low conversions. All condensable vapors were trapped at −196°C, washed into a known volume of solution with acetone, and samples were injected onto the chromatographic columns. All possible products were found to dissolve in acetone, and calibration experiments showed that the method of trapping and analysis was accurate to within the limits of reproducibility of the chromatograph. Samples of permanent gases and carbon dioxide were obtained using an on-line gas sampling valve coupled to the gas chromatograph. This instrument was fitted with a gas density balance and a katharometer detector: organic products were analyzed on columns packed with 10% Carbowax 20M on embacel (5′) or with 10% S.F.96 on acid washed Celite (100/120 mesh:5′). Carbon dioxide was analyzed on a silica gel column. Permanent gases were analyzed on a molecular sieve column (Linde type 5A:3′).

The surface areas of the pumice and of the catalyst were measured in a conventional BET apparatus modified to measure low areas. Best estimates of the surface area of the supported catalyst gave the value 3×10^3 cm^2 g^{-1}.

RESULTS

The stability and life of the molybdenum trioxide catalyst was investigated over a period of 200 hr. Oxygen:toluene mixtures of known composition were passed over the catalyst at long contact times and at a temperature of 450°C, and the products of reaction were analyzed at various stages. No deactivation of catalyst could be observed before 120-hr usage: in all other experiments the catalyst was changed after a maximum of 100 hr usage. The effect of temperature on the yield of major products from the oxidation of toluene was also investigated. At an oxygen:toluene ratio of 3.4 and a contact time of 20-sec, oxidation commenced at ca. 350°C and the produc-

tion of benzaldehyde reached a peak at ca. 460°C. Small amounts of solid products were found in the outlet to the reactor: samples of this product dissolved in sulfuric acid and in o-dichlorobenzene gave the spectra of anthraquinone, and this identification was confirmed by melting point determination and by chemical tests. Only traces of carbon monoxide and benzoic acid could be identified among the reaction products.

Measurements of the kinetics of the oxidation were made with respect to initial rates of reaction and are reported in terms of the power rate law

$$\frac{d(\text{benzaldehyde})}{dt} = k'[\text{toluene}]^x[\text{oxygen}]^y.$$

$$(1)$$

The dependence of rate upon the concentration of one component was ascertained with the other component in excess. Initial rates were determined from plots of product concentration vs contact time, these plots being found to be linear at low contact times and to extend through the origin. Rates were calculated on the basis of residence time of the gas in the catalyst bed at the temperature of the reaction.

The order of reaction was determined from the slope of a plot of log rate vs log [minority reagent]: in some cases where it was not possible to increase the concentration of substituted toluene to an extent where the rate was independent of fuel concentration, the order of the reaction w.r.t. oxygen was obtained from a plot of log rate/[fuel]^x vs log [O$_2$]. Values of reaction order, together with energies of activation obtained from a plot of log k' vs $1/T°$K, are recorded in Table 1.

The Arrhenius plots, which are shown in Fig. 1, show no compensation effects.

The temperature of the catalyst bed was found to be constant within ±2°C during all kinetic investigations. No evidence could be obtained for homogeneous reaction or for mass transfer control of reaction rates. Operation of the reactor filled with pumice alone gave no discernible reaction at 500°C. Calculation of rates of mass transfer gave results considerably faster than the rates

TABLE 1

KINETIC PARAMETERS IN THE OXIDATION OF UNSUBSTITUTED AND SUBSTITUTED TOLUENES

Fuel	Order w.r.t.		Activation energy (kcal mole^{-1})
	Fuel	Oxygen	
Toluene	1.0	0	27.4
o-Chlorotoluene	0.87	0.28	16.9
m-Chlorotoluene	0.94	0.29	17.4
p-Chlorotoluene	0.87	0.27	17.2
o-Xylene	Not measurable		
m-Xylene [het]	0.71	0.40	17.1
[homo]	0.50	0	
p-Xylene [het]	0.75	0.49	18.05
[homo]	0.88	0.74	

of reaction observed (18). Standard tests (19) for bulk and pore diffusion, such as decrease in catalyst pellet size, had no effect on experimental results.

Similar studies have also been completed on the oxidation of chlorotoluenes. Maximum yields of chlorotolualdehyde were again observed at ca. 460°C and chlorotolualdehyde and carbon dioxide were found to be the major products of reaction: no trace of benzaldehyde and only traces of chlorobenzoic acids could be identified. In the case of o-chlorotoluene, solid crystals were observed in the reactor chamber after

some use: these crystals contained neither chlorine nor molybdenum and appeared to be completely organic in nature.

The results of investigation of the dependence of initial rates upon reactant concentration for the three chlorotoluenes are reported in Table 1. No trace of homogeneous reaction, or of mass transfer control of reaction rates was observed. Temperatures in the catalyst bed were found to be constant to ±2°C under conditions of low conversion.

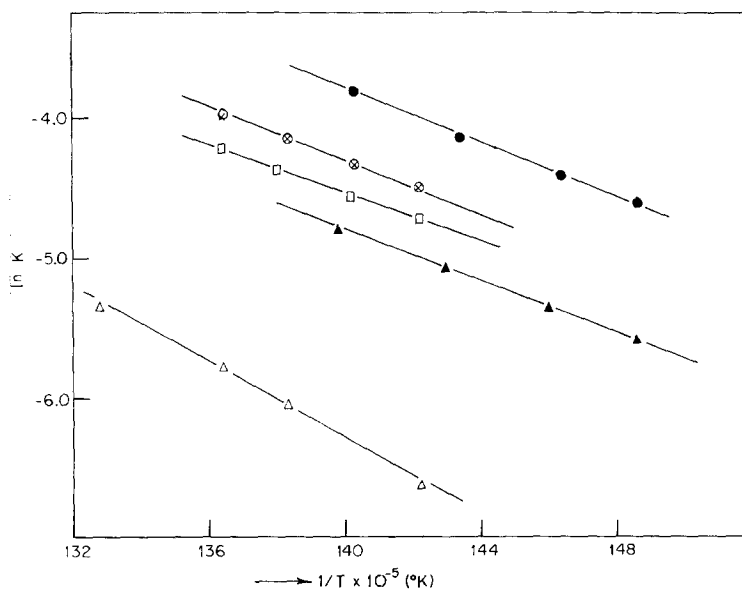Preliminary studies of the catalytic oxidation of o-xylene were carried out at

FIG. 1. Arrhenius plots for the oxidation of unsubstituted and substituted toluenes: △, toluene; ☐, o-chlorotoluene; ⊗, m-chlorotoluene; ○, p-chlorotoluene; ▲, m-xylene; ●, p-xylene.
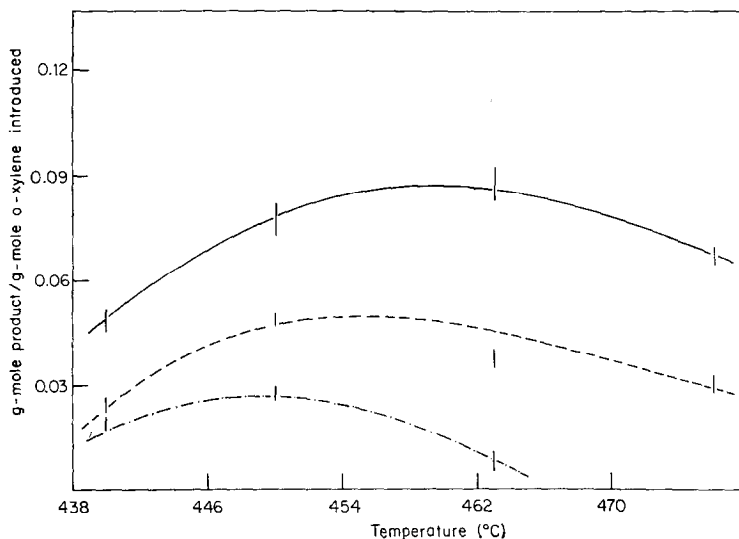
Fig. 2. The oxidation of o-xylene as a function of temperature : oxygen : fuel, 2.8; contact time = 8.7 sec; (————), benzoic acid; (————), o-tolualdehyde; (·—·—·), phthalic anhydride.

460°C using an oxygen:fuel ratio of 2.8. The reaction was much less selective, giving phthalic anhydride, tolualdehyde+phthalan (not separable), benzoic acid, carbon dioxide, traces of maleic anhydride and one unidentified product. Using the same oxygen:fuel ratio, maximum yields of three of the products were obtained at different temperatures (Fig. 2). Experiments were also carried out to investigate the depend-

ence of conversion on oxygen:fuel ratio (Fig. 3) and on contact time (Fig. 4).

Despite very careful attention to the results at low contact time, the plot of conversion vs contact time did not pass through the origin. During these experiments, the temperature of the catalyst bed rose by more than 60°C, and carbon was deposited in the reactor preheater and on the catalyst. Homogeneous reaction was
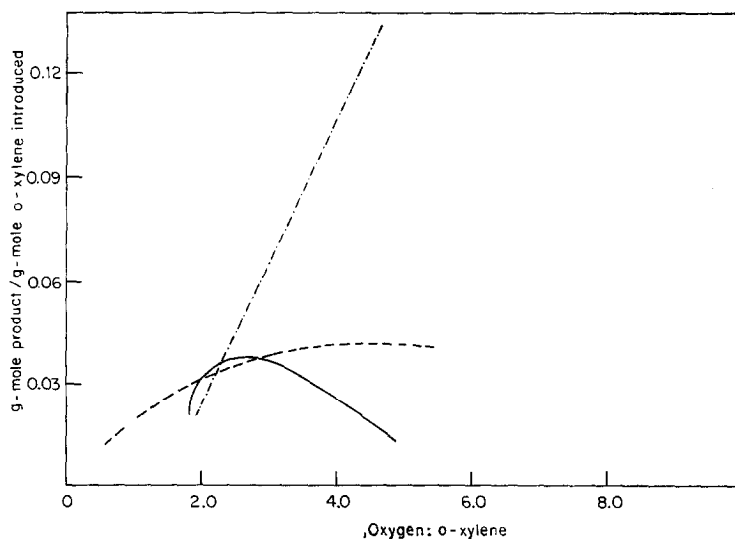

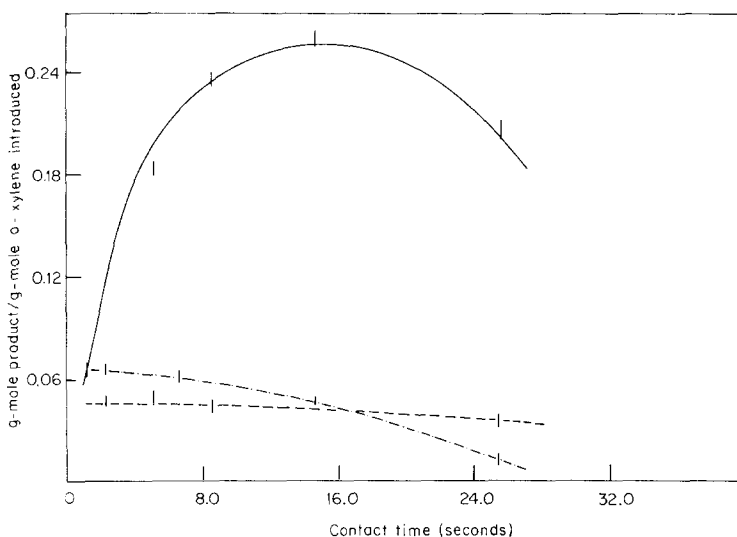Fig. 3. The oxidation of o-xylene as a function of oxygen:fuel ratio contact time, 2.2 sec; temp. 405°C.

FIG. 4. The oxidation of o-xylene as a function of contact time oxygen:fuel, 4.7; temp, 450°C.

suspected and tests with a reactor filled with pumice confirmed that gas phase reactions were so important as not to allow the measurement of the rates of the heterogeneous reaction.

Similar experiments in the absence of catalyst showed that m- and p-xylene could also oxidize in the gas phase at high temperature and oxygen-rich conditions, but only to a small extent. Rates of heterogeneous reactions were obtained as follows: under known conditions the concentration of products were measured as a function of time over the catalyst (rate$_{het+homo}$). Under the same conditions, the experiments were repeated over exactly the same amount of pumice stone (rate$_{homo}$) and the concentration of product subtracted from the (het + homo) concentration and plotted as a function of contact time to give rate$_{het}$. As the concentration of products produced homogeneously is always low (e.g., ca. 1–5% of the corresponding heterogeneous amount) this procedure probably does not introduce any major error. Values of reaction orders and energies of activation obtained for the homogeneous and heterogeneous systems are reported in Table 1. Apart from methyl benzaldehydes no major partial oxidation products were observed. No dialdehydes or diacids were identified and only traces of methyl benzoic acids were observed.

The dependence of the reaction rate on the concentration of oxygen in the case of m-xylene is less accurate than other results as it was not possible to vary the concentration of fuel over a wide range with the present bubbler design for fuel injection (see Experimental Methods).

Samples of the catalyst at various stages during its preparation and life were examined under an electron microscope and under a Stereoscan microscope. The underlying pumice support was seen to be mainly covered by molybdenum trioxide, and the oxide was found to adopt a regular platelet configuration (11) upon activation.
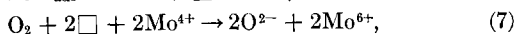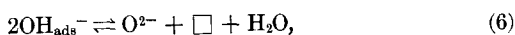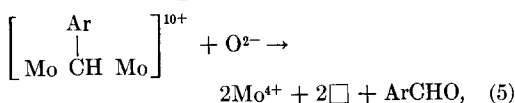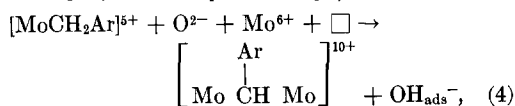
DISCUSSION

a. The Oxidation of Toluene

Molybdenum trioxide was found to be a selective, albeit rather inactive, catalyst for the oxidation of both unsubstituted and substituted toluenes. The catalyst was much more selective than bismuth molybdate (20), oxidation producing the corresponding aldehydes and only small amounts of carbon dioxide (ca. 3% of the toluene oxidized): solid products such as anthraquinone appear to originate from the dimerization of benzaldehyde (21). Only small traces of acidic products were observed.

Although molybdenum trioxide has not

been widely studied as a catalyst in its own right, the behavior of the solid has received some attention in the context of studies of bismuth molybdate catalysts. By analogy with the reaction scheme proposed by Batist *et al.* (*10–12*) for the oxidation of butene over bismuth molybdate, it is possible to describe the catalytic oxidation of toluenes to aldehydes over molybdenum trioxide in terms of the reactions

$$ArCH_3 + \square + O^{2-} \rightleftharpoons ArCH_2^- + OH_{ads}^-, \quad (2)$$

$$ArCH_2^- + Mo^{6+} \rightarrow [MoCH_2Ar]^{5+}, \quad (3)$$

$$[MoCH_2Ar]^{5+} + O^{2-} + Mo^{6+} + \square \rightarrow$$
$$\begin{bmatrix} Ar \\ | \\ Mo\ CH\ Mo \end{bmatrix}^{10+} + OH_{ads}^-, \quad (4)$$

$$\begin{bmatrix} Ar \\ | \\ Mo\ CH\ Mo \end{bmatrix}^{10+} + O^{2-} \rightarrow$$
$$2Mo^{4+} + 2\square + ArCHO, \quad (5)$$

$$2OH_{ads}^- \rightleftharpoons O^{2-} + \square + H_2O, \quad (6)$$

$$O_2 + 2\square + 2Mo^{4+} \rightarrow 2O^{2-} + 2Mo^{6+}, \quad (7)$$
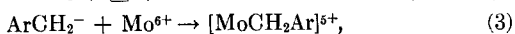
where $\square$ is an anion vacancy at the surface.

The adsorption of toluene has been suggested to involve side chain attachment, largely on the basis of the work of Popova and Kabrakova (*22*) on the oxidation of toluene over copper catalysts, and also in view of the selectivity of the reaction. A similar scheme could be written involving adsorption of toluene via the aromatic nucleus, but complete oxidative degradation in such a system would be expected to be more important than the value indicated by the experimentally observed 3% decomposition of toluene to carbon dioxide. Diadsorbed toluene is suggested to involve two Mo^{6+} centers largely because these ions are known to be close together in the trioxide structure (*11*).

Although adsorbed oxygen species are known to react only as O^{2-} (*4*), the production of aldehyde [reaction (5)] might be suggested to involve gaseous oxygen or diatomic species of the type identified by Cornaz *et al.* (*5*). If such reactions do occur then the results of the kinetic analysis (see below) indicate that they are fast and not rate controlling.

The overall rate of oxidation would appear to be determined by the rate of reaction between toluene and the catalyst, since the initial rate is first order in fuel and is independent of the concentration of oxygen, and is not controlled by the rate of mass transfer in the system. In these circumstances, it is rewarding to compare the present results with those obtained for the reduction of molybdenum trioxide by butene and by hydrogen (*11, 23*). Indeed, if the reaction rate is controlled by the rate of formation of OH_{ads}^-, then the three rates should be very similar. At a temperature of 460°C, the rate constant for the reduction of molybdenum trioxide by butene has been found to be ca. 0.33 sec^{-1} (*11*) and the value for reduction by hydrogen is approximately the same. Assuming that the same value can be used for reduction by toluene, and that O^{2-} reacts both to produce OH_{ads}^- and aldehyde, then the calculation reported by Batist *et al.* (*11*) for butene can be modified for the toluene case to show that the rate of production of benzaldehyde (if the rate of reduction of the catalyst is rate controlling) is 0.0031 cm^3 g^{-1}sec^{-1} at 460°C. Experimental studies of the rate of oxidation of toluene over molybdenum trioxide show that 0.0033 cm^3 g^{-1} sec^{-1} of benzaldehyde are produced at 460°C. The agreement between the two values, bearing in mind the approximation of the calculation, is excellent and the result appears to confirm the suggestion that the overall oxidation of toluene is controlled by the rate of reduction of the catalyst. The reliability of the calculation is not sufficient, however, to confirm the reaction scheme above.

The rate of reduction of the catalyst can be controlled in turn by several factors, which include the rate of production of hydrocarbon ions or the rates of reactions **producing adsorbed hydrocarbon or OH_{ads}^-** Batist *et al.* (*11*) have argued that it is the rate of production of the latter which is rate determining, but this suggestion suffers from the difficulty that the presence of water would be expected to inhibit removal of OH_{ads}^- (reaction 6), and hence the overall oxidation. This prediction has not been confirmed by experimental measurements. Some light can be thrown on this problem

in the toluene oxidation by consideration of the oxidation of xylenes.

The presence of side chain substituents is known to have a marked effect on the electron distribution in an aromatic molecule. Mainly on the basis of liquid phase studies (16), it has been possible to identify the effect of some of these groups. The inductive effect of the methyl group in toluene is known to tend to produce a higher concentration of electrons in the aromatic nucleus, which is concentrated at the *ortho* and *para* positions
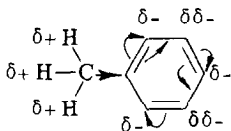
The removal of an H⁺, as is demanded in reaction (2) should be fairly easy. Substitution of a second methyl group *o*- or *p*- to the original substituent would tend, however, to increase the density of electrons at the position in the aromatic nucleus to which the original methyl is attached. Hence, it should be more difficult to remove an H⁺ from the original methyl and the rate of reaction should drop (if the overall rate is dependent upon the rate of production of R⁻ and H⁺) or stay the same (if the overall rate depends on the rate of production of OH$_{ads}$⁻). In fact, the results reported in Fig. 1 show that the rate of oxidation of *p*-xylene is *faster* than that of toluene, even though the rate determining step appears to have changed (Table 1).

These observations can, in fact, only be explained if the formation of the adsorbed complex [ArCH₂Mo]⁵⁺ is rate determining. Any factor which tends to localize change in a position from which it can easily be transferred to a Mo⁶⁺ ion would increase the rate of formation of this complex and hence the overall rate of oxidation. The second methyl group in xylenes—compared with toluene—produces both these effects, and the surprising conclusion emerges that the rate of formation of the adsorbed hydrocarbon is rate determining. Extension of this conclusion to the oxidation of butene over bismuth molybdates removes many of the difficulties associated with the mecha-

nism suggested by Batist *et al.* (11). The fact that data obtained for the reduction of molybdenum trioxide by butene can be used in the toluene system to predict a rate of reaction which is close to the experimentally observed rate would indicate that the same step could well be rate determining in both systems.

b. The Oxidation of Substituted Toluenes

With the exception of *o*-xylene, the oxidation of chlorotoluenes and xylenes was found to be selective and to yield mono-aldehydes and carbon dioxide as major products. Some chlorotoluene did undergo complete degradation, but no trace of chlorine residues could be detected on the catalyst. In particular the crystalline products observed in the reactor after the oxidation of *o*-chlorotoluene were found to be organic, and gave no response to spot tests for molybdenum or chlorine.

Investigation of the initial rates of reaction of the substituted toluenes showed that the systems all obeyed power rate laws in which the dependence of rate upon the concentration of fuel and oxygen was found to be fractional (Table 1), and the energies of activation all fell within the region, $E_A \simeq 17$–18 kcal/mole (cf. toluene, $E_A = 27.4$ kcal/mole). In contrast with the oxidation of xylenes over copper catalysts doped with molybdenum and tungsten oxides [where the rate of cleavage of the C–H bond in the methyl group appeared to be rate determining (24)], these results indicate that a surface reaction is rate controlling. Turning to reactions (2–7) above, then either reaction (4) or (5) must be the slowest reaction in the sequence. The rate of reaction will then depend on the fractional coverage of the surface (θ) by toluene and O²⁻ ions:

$$r = k\theta_T\theta_O$$

Using Langmuir-Hinshelwood arguments, this may be expanded to

$$r = \frac{d(C_T)}{dt} = \frac{kK_TC_T(K_OC_O)^{1/2}}{[1 + K_TC_T + (K_OC_O)^{1/2}]^2} \quad (8)$$

where, K_T, K_O are adsorption equilibrium constants for toluene and oxygen respec-

tively, and $C_{T,0}$ is the corresponding concentration. Taking $(d(C_T)/dt)(1/C_T) = \alpha$, this may be rearranged to give

$$\alpha^{-1/2} = \frac{1 + K_T C_T + (K_O C_O)^{1/2}}{k^{1/2} K_T^{1/2} K_O^{1/4} C_O^{1/4}}. \quad (9)$$

If this equation is applicable to the oxidation of substituted toluenes, then a plot of $\alpha^{-1/2}$ vs C_T should be a straight line of slope $K_T^{1/2}/k^{1/2} K_O^{1/4} C_O^{1/4}$ and intercept

$[(1/k^{1/2} K_T^{1/2} K_O^{1/4} C_O^{1/4})$
$\qquad + (K_O^{1/4} C_O^{1/4}/k^{1/2} K_T^{1/2})]$,

while a plot of $C_O^{1/4} \alpha^{-1/2}$ vs $C_O^{1/2}$ should also be a straight line of slope $K_O^{1/4}/k^{1/2} K_T^{1/2}$ and intercept

$[(1/k^{1/2} K_T^{1/2} K_O^{1/4}) + (K_T^{1/2} C_T/k^{1/2} K_O^{1/4})]$.

As shown in Figs. 5 and 6 these plots are indeed straight lines, although the second plot for m-xylene is restricted by lack of data (see Results). Thus it would appear that Eq. (8) is a true representation of the kinetics of the oxidation, and can be used

to calculate K_T and K_O. The values so obtained are listed in Table 2.

Since all experiments were completed on the same catalyst, values of K_O would be expected to be the same in all cases. On this basis, the results for m-xylene look significantly out of place.

It should be noted that the Langmuir-Hinshelwood equation was developed from a knowledge of the chemistry of the reaction, and confirms the conclusion that reaction (4) involves monatomic oxygen reacting with adsorbed toluene. Although it is often unrealistic to distinguish between reaction mechanisms on the basis only of comparing experimental results with alternative Langmuir-Hinshelwood equations (the experimental error may be of the same order as the difference between results predicted by different theoretical equations), attempts were made to test experimental data against theoretical equations derived on the basis of other rate determining reactions. Langmuir-Hinshelwood equations, de-
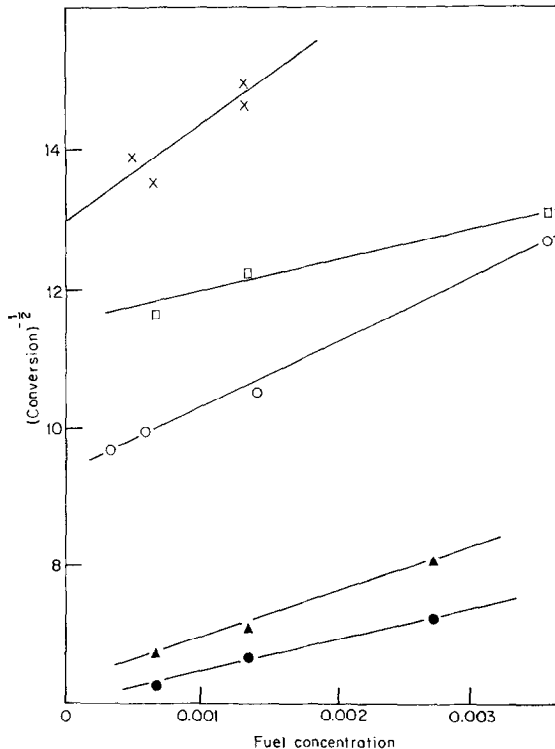

FIG. 5. Langmuir-Hinshelwood plots for the oxidation of toluenes and xylenes: △, toluene; □, o-chlorotoluene; X, m-chlorotoluene; ○, p-chlorotoluene; ▲, m-xylene; ●, p-xylene.
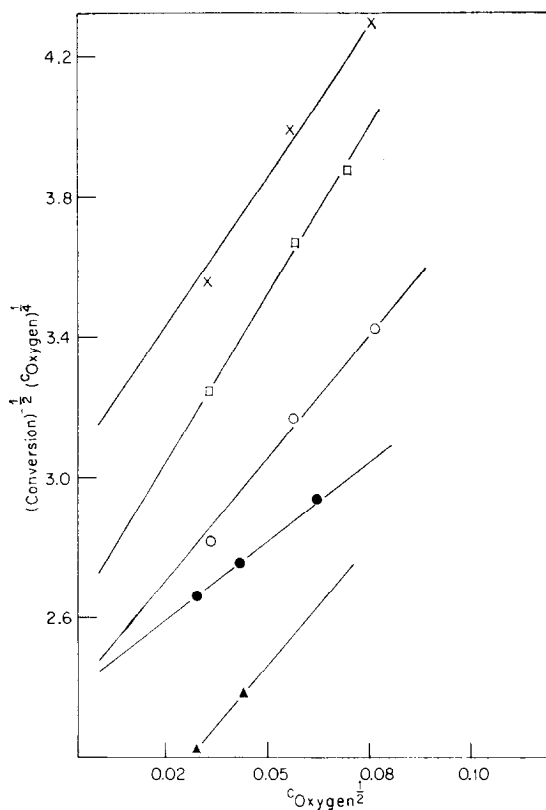
FIG. 6. Langmuir-Hinshelwood plots for the oxidation of toluenes and xylenes.

rived on the basis of, e.g., surface reaction between adsorbed toluene and gas phase or diatomic adsorbed oxygen (5), were not comparable with experimental results. The only satisfactory agreement that could be observed was with the theoretical predictions expressed in Eq. (8).

It is now possible to consider the effect of electron directing substituents on the rate of the surface reaction. In terms of the power rate law, where apparent orders of reaction of zero and unity indicates strong

and weak adsorption, respectively, the order of decreasing strength of adsorption is found to be m-xylene $\sim p$-xylene $> o$-chlorotoluene $\sim p$-chlorotoluene $> m$-chlorotoluene $>$ toluene, and calculated values of K_T (Table 2) follow roughly the same order. This result is very surprising in view of the fact that nitration studies indicate that methyl and chloro substituents should have an opposite effect on the density of electrons in the aromatic ring (16). Since the reactivity of a given system depends on the ease of the surface reaction, which is related to the strength of adsorption of the hydrocarbon, methyl and chloro substituents should have a very different effect on the rate of reaction.

This apparent anomaly can be explained by consideration of the factors influencing electron distribution in the chloro-substituted toluenes. During nitration, the patterns of activity are caused by a combination of an inductive ($-I$) effect and an electromeric effect (16). The importance of this latter effect is, however, very dependent on the external applied field, which will be very different in the vicinity of the Mo^{6+} ion compared to a nitrating reagent. As a result, the electromeric effect will become much more important over a molybdenum trioxide catalyst, and electrons will be moved into the aromatic ring, overcoming the tendency of the $-I$ effect to remove charge. Methyl groups, which have no lone pairs of electrons, will not be affected by an external applied field. In these circumstances, chloro and methyl substituents could well affect the behavior of molecule in the same direction and to approximately the same extent.

Since both substituents have the effect of

TABLE 2
VALUES OF THE LANGMUIR-HINSHELWOOD RATE PARAMETERS AND SUBSTITUENT CONSTANTS

Compound	K_T	K_O	$k \times 10^{-4}$	$\log k$	σ
o-Chlorotoluene	67.3	63.8	4.50	-3.347	$+0.20$
m-Chlorotoluene	145.4	37.1	2.12	-3.675	$+0.37$
p-Chlorotoluene	139.4	53.3	3.90	-3.409	$+0.27$
m-Xylene	350.8	408	3.46	-3.460	-0.07
m-Xylene (calc)	288.3	52.5	7.76	-3.110	-0.07
p-Xylene	135.2	39.5	8.4	-3.076	-0.15

increasing the aromatic electron density and of localizing charge in a position from which electron transfer is possible [this effect will be greatest for substituents *o*- or *p*- to the methyl involved in the reaction, but will also occur with *m*-substituted groups (*16*)], formation of the adsorbed complex $[MoCH_2Ar]^{5+}$ will be easy and breaking of the surface adsorbate bond [reaction (*5*)] will be more difficult. The order of reactivity observed for the oxidation of toluenes where the surface reaction is rate controlling is consistent with these predictions.

In this case, it should also be possible to develop linear free energy relationships for the catalytic oxidation of toluenes of the type suggested by Hammett (*25*) and by Taft (*26*), viz:

$$\log(k/k_O) = \sigma\,\rho, \qquad (10)$$

where k is the rate constant for a side chain reaction of a substituted benzene system and k_O is the value for the parent compound. The substituent constant, σ, reflects the polar effect of the substituent while ρ, the reaction constant, depends on the nature of the particular reaction. Taft has suggested that the value of σ should contain a reaction dependent and a reaction independent term: actual values (*27*), which have been suggested on the basis of results in a large number of systems, are reported in Table 2.

Since the oxidation of toluene is controlled by a different reaction, it is pointless to correct values of k (Table 2) for the value of K_O. However, for a given series involving the same parent, a plot of log k vs σ should give a straight line of slope $\rho \times$ log k_O (Fig. 7).

As shown, the plot is linear, with the exception of the *m*-xylene results which are known to be subject to some inaccuracy. Under the correct conditions then, arguments pertinent to electron transfer reactions in the liquid phase can be applied directly to similar gas–solid catalytic systems.

It is interesting to use Fig. 7 to predict true adsorption equilibrium constants for *m*-xylene. The value of k *m*-xylene, pre-
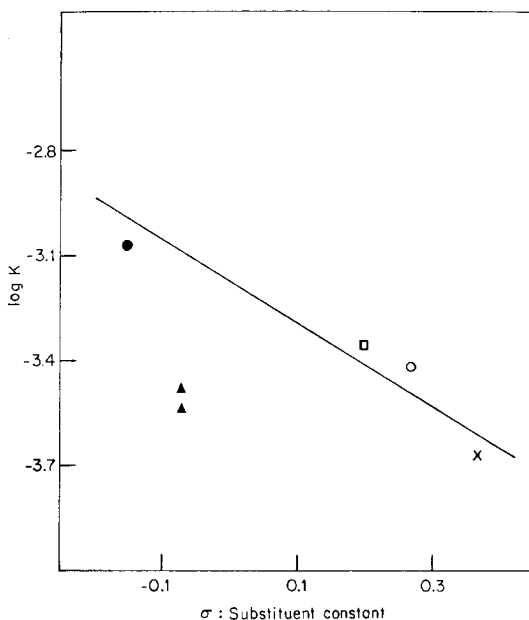

FIG. 7. Plots of the Hammett equation for the oxidation of substituted toluenes: □, *o*-chlorotoluene; X, *m*-chlorotoluene; ○, *p*-chlorotoluene; ▲, *m*-xylene; ●, *p*-xylene.

dicted from this graph, is used together with an average value of K_O (Table 2) in the graph of $\alpha^{-1/2}$ vs C_T (Fig. 5) to predict values of K_T (Table 2). The plot of $C_O^{1/4}\alpha^{-1/2}$ vs $C_O^{1/2}$ was not used to obtain two further values of K_T as the error in the *m*-xylene results is known to be primarily associated with this graph. The values of K_T calculated for *m*-xylene fall in the range expected on the basis of the values in Table 2.

The energies of activation of the apparent rate constants for the oxidation of substituted toluenes might also be expected to mirror the electron directing influence of substituent groups. In fact, all values are surprisingly similar (Table 1) and no compensation effects were observed (Fig. 1). The explanation of this latter observation (*8*), that the energy of activation depends primarily on the entropy of activation, may well be correct under conditions where values of K_T and reaction order are so similar.

The principle that electron directing influences in the hydrocarbon fuel may have a large effect on a catalytic oxidation has

wide application. In addition to direct studies of the influence of substituents on the oxidation of naphthalene (15), patterns of activity of olefin oxidation over nickel oxide (13) and of xylene oxidation over copper catalysts containing heavy metal oxides (24) both show evidence that electron directing factors are influencing the course of reaction. The application of linear free energy relationships of the type illustrated in Fig. 7 may well allow prediction of catalyst behavior in alternative oxidation reactions.

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