JOURNAL OF CATALYSIS 39, 437–448 (1975)

# Oxidation of Toluene over Bismuth Molybdate Catalysts

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Received June 28, 1974; revised April 21, 1975

The oxidation of toluene by air has been studied over a silica-supported Bi–Mo–P–O catalyst (commercial Ketjen "A" catalyst) and over pure bismuth molybdate. All experiments were performed in a continuously operated fixed-bed microreactor at temperatures between 450 and 550°C.

The main part of the study concerned the kinetics of the oxidation of toluene over pure bismuth molybdate. Conversion and product distribution were measured at various space-times, toluene and oxygen partial pressures and temperatures. Benzaldehyde, benzene and carbon oxides were the only important products formed. Except for traces of benzoic acid and anthraquinone no other carbon containing products could be detected. Introductory kinetic measurements indicated a Mars–Van Krevelen mechanism. A set of rate equations, based on a redox mechanism, was derived for the reactions involved. This set of equations gave a satisfactory fit to all the experiments performed.

## INTRODUCTION

Selective vapor-phase oxidation of hydrocarbons, using air as the oxidizing agent, has attracted much attention in the last 20 yr, as is obvious from the great number of articles that has been published in this field. Most of them concern olefins (up to $C_4$); the oxidation products are mainly epoxides, acids, aldehydes, alcohols and products resulting from dehydrogenation. As to the vapor-phase oxidation of aromatic hydrocarbons, successful industrial applications all concern the production of acid anhydrides by oxidation of the aromatic ring, or combined oxidation of two side chains (i.e., *o*-xylene).

Because the present development of new types of catalyst may lead to economically attractive vapor-phase processes for selective side chain oxidation or ammoxidation of aromatic hydrocarbons, the production of benzaldehyde from toluene has been chosen as a model reaction for study of oxidation kinetics and methods to predict optimum reactor design and operation conditions in which a complex reaction system is involved.

Selecting a suitable catalyst for this type of oxidation is a difficult problem. It is clear that a choice should be made in the category of "mild" catalysts, which are mainly metal oxides or metal oxide mixtures. Germain and Laugier (*1–3*) have reported the oxidation of toluene over a series of oxides and mixtures of oxides. The mixtures Fe–Mo, U–Mo and Bi–Mo give the best results, exhibiting both good activity and selectivity. Relating the selectivity and activity to fundamental properties of the catalyst has been the subject of a number of studies (*4–14*). Although important progress has been made in this field selection of a suitable catalyst on a theoretical basis is still problematic, especially for the mixed oxide catalysts.

For the toluene oxidation studied here bismuth molybdate has been chosen as the catalyst because of its remarkable properties in ammoxidation and because much is known about the catalyst itself from other studies (*15–29*).

In this paper the kinetic study of the oxidation of toluene is reported and methods in kinetic modeling and parameter estimation are discussed. A parallel study, concerning pulse experiments, is revealing more about catalyst behavior and mechanisms. It will be reported later.

## METHODS AND RESULTS

### Materials and Catalysts

All gases (helium, nitrogen, air, carbon monoxide, carbon dioxide) were obtained from cylinders and no further purification was found necessary. Analytical grade toluene, benzene and benzaldehyde were used.

Two catalysts have been studied:

1. Ketjen "A" ammoxidation catalyst: a mixture of oxides of bismuth, molybdenum and phosphorus supported by silica (atomic ratio Bi/Mo/P/Si, approx 2:2.5:0.2:14). Irregular shaped particles of 3–8 mm diameter were crushed and sieved. A sieve fraction of 0.8–1.0 mm was used in most experiments.
2. Pure bismuth molybdate: this catalyst was prepared in the laboratory of Professor G. C. A. Schuit (Eindhoven University of Technology). The method of preparation is reported by Batist *et al.* (*19*). The atomic ratio Bi/Mo was 2:1.3, which means some excess of $MoO_3$ with respect to koechlinite ($Bi_2O_3 \cdot MoO_3$).

A sieve fraction of 0.35–0.85 mm was used in all experiments. Crushed quartz of the same sieve fraction served as diluting material.

### Apparatus

Except for the control unit for gas flows the entire apparatus is made of stainless steel 316. The reactor consists of a tube (inner diameter, 6 mm), which is externally heated by a fluidized bed of silicon particles to assure good heat exchange and isothermal reaction conditions. Toluene, benzene or benzaldehyde are introduced to the feed gas stream by passing a part of the stream through a saturator contained in a thermostat. Bubbles are formed in a sintered porous stainless steel plate at the bottom. At a liquid height of 30 cm saturation is complete. Problems mentioned by Trimm and Irshad (*30*) do not occur. A constant feed of any desired composition can be adjusted. Feed and product can be sampled during continuous operation by a combination of two valves (both "Ratfisch" 6-way valves with a strengthened Teflon slider) and one sample loop. The valves are placed in an air thermostat (200°C).

The analysis system allows quantitative determination of benzene, toluene, benzaldehyde, nitrogen, oxygen, carbon dioxide, carbon monoxide and water. The system consists of three GSC-columns in series connection and thermal conductivity detectors after each of the columns. On the first column (0.4 m Porapak Q, 190°C) the aromatic products are separated. On the second column (2 m Porapak Q, 60°C) carbon dioxide and water are detected, while oxygen, nitrogen and carbon monoxide are determined on the third column (molecular sieve Linde 5A). Helium is used as carrier gas, at a flow rate of 30 $cm^3$/min, which demands a pressure of 1 atm gauge. The nitrogen peak is used as an internal standard, since nitrogen is not affected in the oxidation reactions.

In a condenser (−77°C), hydrocarbon vapors from the reactor product stream can be trapped for sensitive qualitative analysis of oxidation products.

### Program of Experiments

#### *Qualitative Experiments*

Before quantitative experiments were started a series of qualitative experiments was carried out to insure that the kinetic experiments gave meaningful results. Oxidations were performed under various conditions to study the main oxidation products formed. Thermal oxidation of toluene and benzaldehyde was investigated in the empty reactor. Catalytic oxidation of benzaldehyde and benzene were studied. Catalyst particle diameter was varied to check absence of internal diffusion limitations. The activity and stability of the catalyst were determined to find an appropriate catalyst pretreating procedure. Most of these experiments were carried out on both the supported and the pure bismuth molybdate catalyst.

### *Introductory Kinetic Experiments*

The pure bismuth molybdate catalyst was selected for a kinetic study. To investigate the type of kinetic model suitable for this oxidation, experiments were carried out at various feed compositions, including a mixed feed of toluene and benzaldehyde.

### *Kinetic Experiments*

Since the oxidation of toluene is highly exothermic special attention has been given to possible and undesirable temperature profiles in the catalyst bed. Experiments were carried out with a thin (0.5 mm) thermocouple at varying positions on the axis of the catalyst bed. Dilution of the catalyst with an equal volume of inert material (quartz) guaranteed sufficient isothermal conditions.

Series of experiments were carried out in which temperature, space-time, toluene and oxygen partial pressure were varied one or two at a time. All these experiments together were used to estimate kinetic model parameters.

## Results of Qualitative Experiments

The products of catalytic and thermal oxidation have been studied under various conditions. Catalytic oxidation of toluene led to benzaldehyde, benzene and carbon oxides as the main products, besides traces of anthraquinone and benzoic acid. Thermal oxidation of toluene was negligible under comparable conditions. The catalytic oxidation of benzaldehyde was faster than the toluene oxidation. The same products were formed; anthraquinone, however, was found in much larger quantities. The thermal oxidation of benzaldehyde was slow compared with the catalytic oxidation. Remarkably, only carbon oxides were found and no anthraquinone. Both catalytic and thermal oxidation of benzene were negligible under toluene oxidation conditions.

Qualitatively there was not much difference in catalytic behavior between the supported and the pure bismuth molybdate catalyst. About the same selectivities were measured. The pure bismuth molybdate had a higher activity per gram of catalyst.

### *Catalyst Activity and Stability*

The catalysts were active without any pretreatment. There was no significant difference in activity when the catalyst was pretreated by an air stream at various temperatures up to 570°C and during 24 hr. However, a significant decrease in activity occurred during the first period of experimentation with a fresh catalyst. A typical example is shown in Fig. 1. After a period of 30 hr the activity was practically constant. The length of this period and the final activity level were dependent on temperature and the ratio $W/F$ (catalyst weight/mass flow toluene fed to the reactor). Therefore a 50 hr run at standard conditions was used as the catalyst pretreatment before kinetic investigations were started. As Fig. 1 shows, the benzene formation was only important on a fresh catalyst. The benzene production steadily decreased and became less than 1% after 50 hr. Therefore benzene has been excluded in the kinetic model developed here. Decreasing conversion and increasing selectivity towards benzaldehyde are probably both effects of decreasing activity and are not caused by other changes in

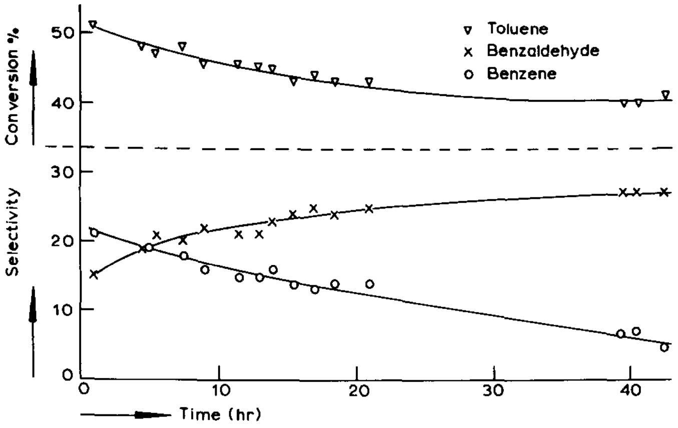


FIG. 1. Deactivation of a fresh catalyst.

catalyst properties. This is discussed below.

## Introductory Kinetic Experiments

The aim of these experiments was to obtain enough information to be able to discriminate between possible kinetic schemes and models. Because benzaldehyde and carbon oxides were considered as the only products of oxidation, the first thing to determine was whether the oxidation of benzaldehyde was important, and whether direct oxidation of toluene to carbon oxides took place.

The importance of benzaldehyde oxidation is shown in Fig. 2, representing two experiments in which the feed consisted of air and relatively small amounts of toluene or benzaldehyde. Space-time was varied, and because of the excess of air the reaction rate was assumed first order in the aromatic reactant. This assumption is confirmed by the straight lines in Fig. 2. The ratio of the slopes of these lines indicates that benzaldehyde is oxidized approximately three times faster than toluene.

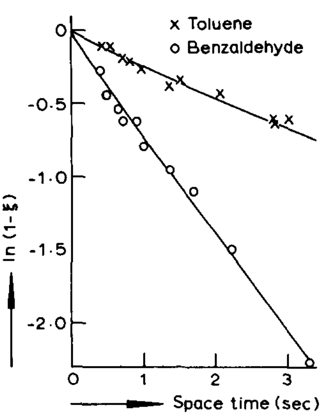


FIG. 2. Comparison of toluene and benzaldehyde oxidation rates ($\xi$ = conversion).

The direct oxidation of toluene has become clear from a series of experiments represented in Figs. 3 and 4. Toluene was oxidized with air at various space-times and three temperature levels. Figure 3 shows the dependence of selectivity on conversion. Remarkably all measurements are fitted by one curve. The form of the curve leads to the first conclusion: 40–50% of the toluene is directly oxidized, since the initial selectivity is 50–60%. The

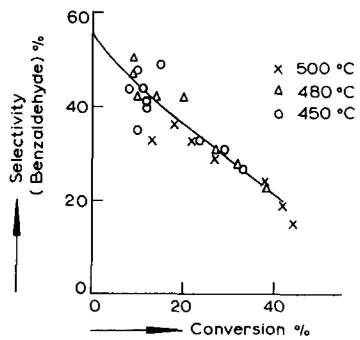


FIG. 3. Selectivity as a function of conversion.

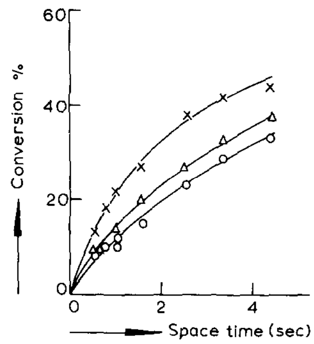
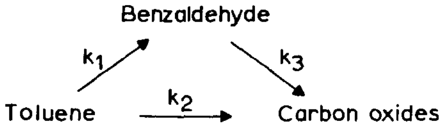


FIG. 4. Conversion versus space-time at 500, 480, 450°C.

curve in Fig. 3 is a calculated curve for the kinetic scheme shown below:



The ratio of the first order rate constants $k_1:k_2:k_3$ was set to the value 0.55:0.45:3, to produce the best fitting line. The fact that all measurements fit the same curve leads to the second conclusion: the activation energies of the three reaction steps have approximately the same magnitude, since the influence of temperature on the selectivity-conversion pattern is small. This conclusion is confirmed by our pulse experiments.

The reaction kinetics cannot be described by first order dependency in aromatic reactants only. Figure 5 shows the results of the oxidation of toluene when only a small excess of air is present. Now no linear plot is found as in Fig. 2. Hence oxygen must play a role in the kinetics. The same can be concluded from the oxidation of toluene at varying oxygen partial pressures and constant space-time (Fig. 6). Decreasing the oxygen/toluene ratio strongly influenced the conversion of toluene, although the oxygen conversion remained far from 100%.

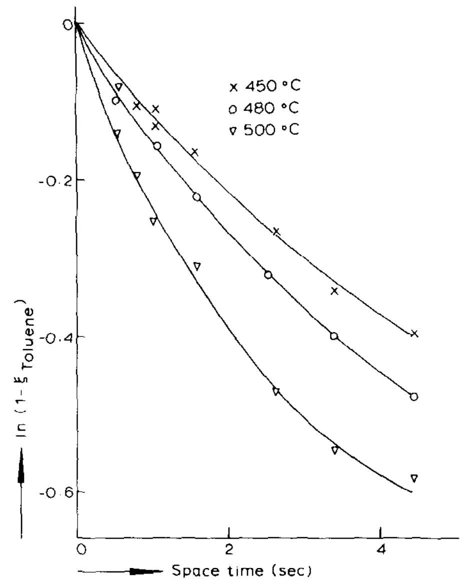


FIG. 5. Deviation from simple first order kinetics ($\xi$ = conversion).

Product inhibition does not play any role here. This can be concluded from the fact that benzaldehyde was rapidly oxidized and from experiments with a mixed feed of toluene and benzaldehyde. No significant influence of benzaldehyde on toluene conversion was found.

## Design of a Kinetic Model

From three types of kinetic equations, the power equation, the Hougen and Watson models and the Mars and Van Krevelen (*31*) model the latter has been chosen. At an early stage of the investigations, when attempts were made to describe the toluene oxidation as one overall

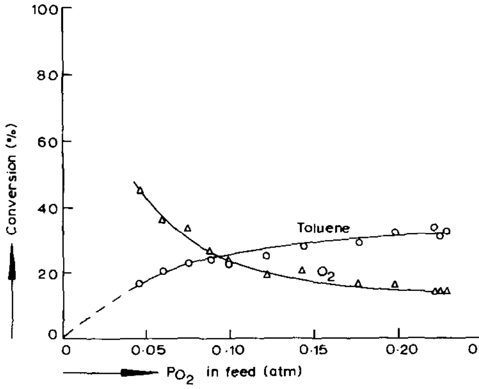


FIG. 6. Influence of oxygen partial pressure on conversion.

reaction, the Mars and Van Krevelen model turned out to be successful. According to this model the oxidation rate of toluene is given by:

$$R_{\text{tol}} = \frac{1}{(1/k_t \cdot P_{\text{tol}}) + (n_{\text{O}}/k_{\text{O}} \cdot P_{\text{O2}})}, \quad (1)$$

in which $n_{\text{O}}$ is the average number of moles oxygen consumed by oxidation of 1 mole toluene. Substitution of $-dp_{\text{tol}}/d\tau_s$ for $R_{\text{tol}}$ and application of the mass balance $dp_{\text{O}_2} = n_{\text{O}} \cdot dp_{\text{tol}}$ leads, after integration and rearrangement, to an equation also given by Mars and van Krevelen:

$$-\frac{\tau_s}{\ln(1-\xi_{\text{tol}})} = \frac{1}{k_t} + \frac{1}{k_{\text{O}}} \cdot \frac{\ln(1-\xi_{\text{O}_2})}{\ln(1-\xi_{\text{tol}})}, \quad (2)$$

in which $\tau_s$ is the space time in the reactor and $\xi$ stands for conversion. The same experimental data used in Fig. 3 are presented in a plot of $-\tau_s/[\ln(1-\xi_{tol})]$ vs $[\ln(1-\xi_{\text{O}_2})]/[\ln(1-\xi_{\text{tol}})]$ (Fig. 7). The straight lines found in this plot indicate that the type of model is correct. Obviously, the reaction rate model in the simple form of Eq. (1) cannot adequately describe the three reaction steps involved. However, the principles of the redox mechanism, which is the basis of the Mars and Van Krevelen model, can be applied very well to this reaction system and worked out on the basis of the following assumptions: Toluene reacts with an oxidized site of the catalyst. The rate of reaction is proportional to the toluene partial pressure and the fraction of oxidized sites $\theta_{\text{O}_2}$:

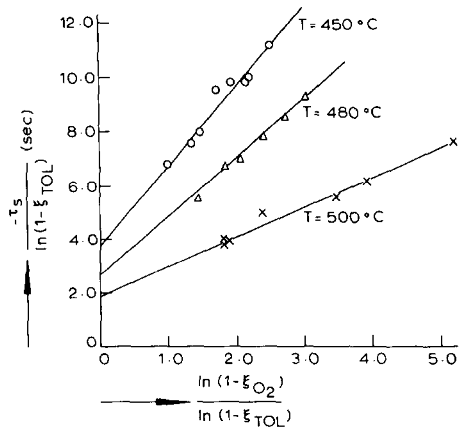


FIG. 7. Plot according to Mars and Van Krevelen model as presented in Eq. (2) ($\tau_s$ = space-time; $\xi$ = conversion).

$$R_{\text{tol}} = -k_t \cdot p_{\text{tol}} \cdot \theta_{\text{O}_2}. \quad (3)$$

Benzaldehyde (ben) reacts in a similar way:

$$R_{\text{ben}} = -k_3 \cdot p_{\text{ben}} \cdot \theta_{\text{O}_2}. \quad (4)$$

Oxygen reacts with reduced sites of the catalyst. The rate of reaction is proportional to the oxygen partial pressure and the fraction of reduced sites on the catalyst:

$$R_{\text{O}_2} = -k_4 \cdot p_{\text{O}_2} \cdot (1 - \theta_{\text{O}_2}). \quad (5)$$

To describe the production of benzaldehyde from toluene, the reaction rate constant, $k_t$, is split into two parts, $k_1$ and $k_2$, $k_1$ concerning oxidation to benzaldehyde and $k_2$ concerning direct oxidation to carbon oxides:

$$k_t = k_1 + k_2. \quad (6)$$

From Eqs. *3–6* the differential equations for an ideal plug flow reactor can be derived:

$$-\frac{d_{\text{tol}}}{d\tau_s} = (k_1 + k_2) \cdot p_{\text{tol}} \cdot \theta_{\text{O}_2}, \quad (7)$$

$$-\frac{dp_{\text{ben}}}{d\tau_s} = (k_3 \cdot p_{\text{ben}} - k_1 \cdot p_{\text{tol}}) \cdot \theta_{\text{O}_2}, \quad (8)$$

$$-\frac{dp_{\text{O}_2}}{d\tau_s} = k_4 \cdot p_{\text{O}_2} \cdot (1 - \theta_{\text{O}_2}), \quad (9)$$

in which $\tau_s$ is the space time in the reactor. The variable $\theta_{\text{O}_2}$ is eliminated by means of the oxygen mass balance:

$$\frac{dp_{\text{O}_2}}{d\tau_s} = \frac{(n_3 + 1) \cdot k_1 + n_2 \cdot k_2}{k_1 + k_2} \cdot \frac{dp_{\text{tol}}}{d\tau_s} + n_3 \cdot \frac{dp_{\text{ben}}}{d\tau_s}, \quad (10)$$

TABLE 1
SUMMARY OF EXPERIMENTS

| No. of series | Variable | Reaction conditions: Feed composition $p_{\mathrm{tol}}$ | Feed composition $p_{O_2}$ | Space-time (sec) | Temp (°C) |
|---|---|---|---|---|---|
| 4 | Space-time | 0.075 | 0.20 | 0.5–5.0 | 450<br>480<br>500 |
| 3 | $p_{O_2}$ | 0.02 | 0.05–0.20 | 1.0 | 500 |
| 2 | $p_{\mathrm{tol}}$ | 0.002–0.15 | 0.20 | 1.0 | 500 |
| 1 | $p_{\mathrm{tol}}$ and $p_{O_2}$ | 0.02–0.08 | 0.20–0.02 | 1.0 | 500 |

Total No. of experiments, 110

in which $n_2$ stoichiometric constant: number of moles oxygen consumed by oxidation of 1 mole benzaldehyde (reaction step 2)

$n_3$ stoichiometric constant: number of moles oxygen consumed by total oxidation of 1 mole toluene (reaction step 3)

Then the system of differential equations can be solved for any set of $k$-values by numerical integration.

## Kinetic Experiments

To check whether the assumed kinetic model could fit the measurements correctly and to determine accurate values of rate constants a large number of experiments were carried out. A summary is given in Table 1. The results of these experiments will not be presented in detail. Three typical examples of experimental series are shown in Figs. 8–10. The solid curves result from calculations described below.

### *Method of k-Values Estimation*

The $k$-values were estimated by a nonlinear regression technique, which involves minimization of the sum of squares of deviations (between measured and calculated partial pressures) with respect to the $k$-values by a general minimization proce-

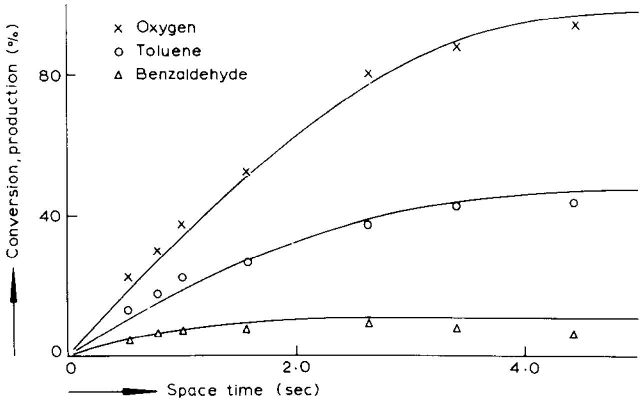


FIG. 8. Reactor performance at varying space-times (data points and calculated curves).

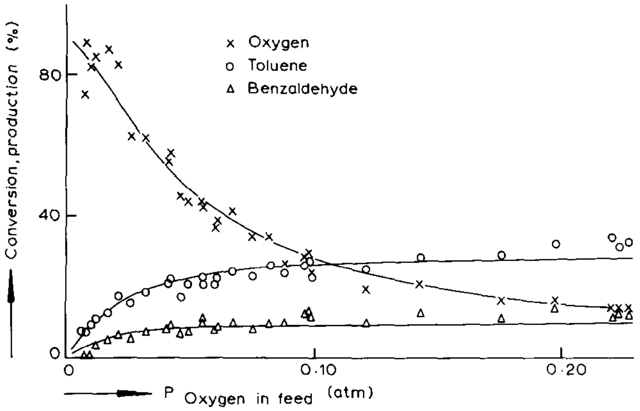


FIG. 9. Reactor performance at varying oxygen partial pressure (data points and calculated curves).

dure (*32*). Powell's minimization routine was used, available at the University's Computer Centre (*34,35*). Three problems complicated the regression for the model and the data presented here:

a. The model is a multiresponse model [three partial pressures are measured, Eqs. (7)–(9)].

b. The variance of experimental error is not a constant.

c. The estimated *k*-values are strongly interdependent in some cases.

Concerning (a), the interdependence of the three responses was first ignored, but accounted for later, by applying the method of Box and Draper (*33*). However, the influence of this refinement was small and is not reported here.

With regard to (b), this problem was solved by using appropriate weight factors, calculated from independent estimates of the experimental error variance.

As to (c), in the first instance calculation of *k*-values was individually tried for each series of experiments. Good results were obtained for the first 4 series (Table 1). There was good agreement between the ratio of *k*-values. (Once more it turned out that there was no significant influence of temperature on the ratio of *k*-values. Even the reoxidation reaction seemed to have an activation energy close to those of the oxidation reactions.) However, as to the other series there was no good agreement between *k*-values. At the same time a relatively large (combined) variation of these values did not much influence the fit, indicating a strong interdependence of *k*-

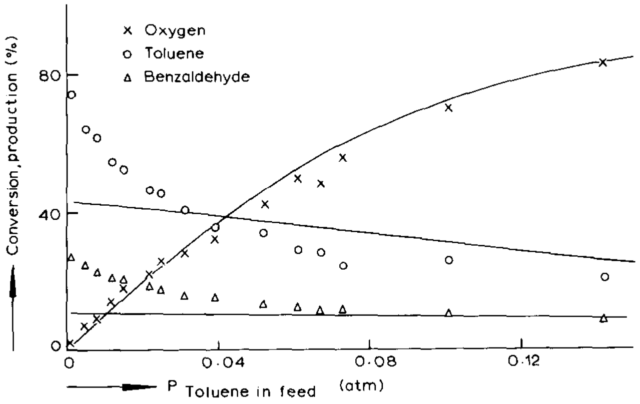


FIG. 10. Reactor performance at varying toluene partial pressure (data points and calculated curves).

values. This dependency is inevitable in nonlinear regression, and especially large when a regression variable (or combination of regression variables) is almost constant within a series of experiments, which is the point here. This problem can be overcome by taking together all experimental series (in which different conditions were varied one at a time) and by performing a single combined regression. This is not very simple, however. The catalyst activity, and thus the level of $k$-values, varies because different temperatures were used and because careful catalyst pretreatment could not prevent some difference in activity between subsequent reactor fillings. Nevertheless, combination of all series is possible, if variation of catalyst activity is assumed not to influence significantly the *ratio* of $k$-values. Therefore a two-step regression procedure was constructed, schematically shown in Fig. 12. The "master" search routine determines the best fitting *ratio* of $k$-values for all series together, while the "slave" search routine calculates the optimum *level* of $k$-values for each individual series. This procedure was applied to all series of experiments listed in Table 1 together, and gave good results.

## Results of Regression Calculations

The results are shown in Table 2, and the good quality of fit is demonstrated in Figs. 8–10. The quality of the fit has not significantly decreased compared with individual series regressions. This means that the assumption of constant $k$-value ratios is reasonable.

TABLE 2

FINAL RESULTS OF KINETIC PARAMETERS

| Mean values | |
|---|---|
| Rate constants ($s^{-1}$) | |
| $k_1$ | 0.20 |
| $k_2$ | 0.17 |
| $k_3$ | 1.0 |
| $k_4$ | 2.6 |
| Activation energy | |
| $E_A$ (kcal/mole) | 16 |
| SD[a] (%) | 25 |

[a] Standard deviation of the variation of the level of $k$-values.

Lack of fit might be concluded for the region of very low toluene partial pressure (less than 2% toluene in the feed), because large deviations are visible in the left part of Fig. 10. It is not certain, however, that these deviations have not been caused merely by experimental error. Notice that in Fig. 10 conversion and production percentages are plotted, while partial pressures in feed and product are the variables that were measured and used in the regression, as presented in Fig. 11. Relatively small errors in measured partial pressures

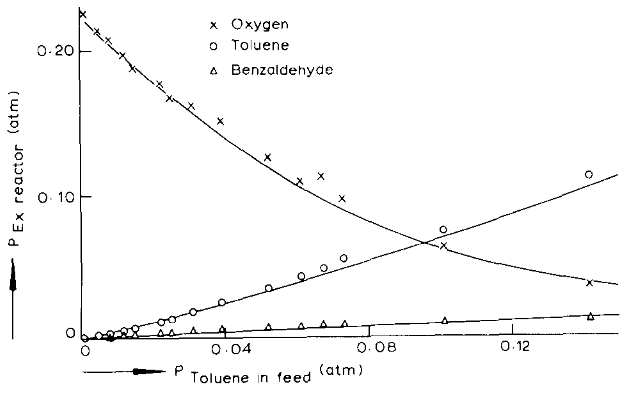


FIG. 11. Product distribution at varying toluene partial pressure (data points and calculated curves).

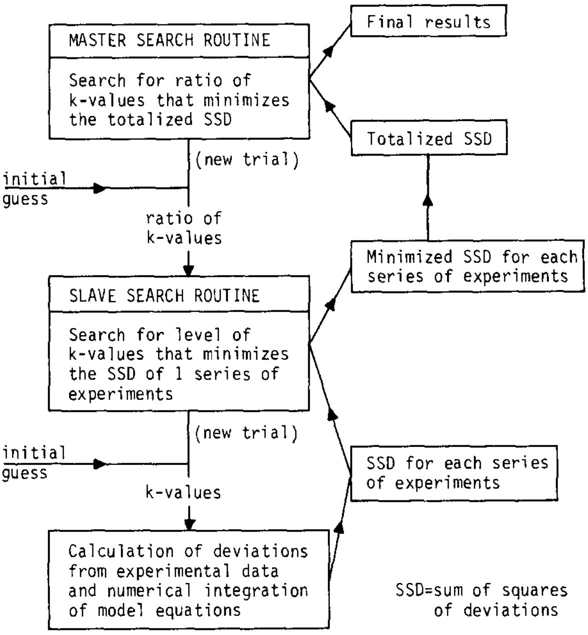


FIG. 12. Diagram of the two-step regression procedure.

cause remarkably large deviations in conversions and production percentages.

The assumption that the reaction order with respect to oxygen should be 1 was confirmed: a value of 1.05 resulted when a regression was performed in which both the *k*-values and the oxygen reaction order were used as parameters. Moreover the next probable value (0.5) was tried to check whether the model is sensitive to this parameter. A significant decrease in the quality of fit resulted.

## DISCUSSION

### *Product Spectrum*

The observations are in good agreement with the results of Germain and Laugier (*3*), who oxidized toluene over bismuth molybdate at 400°C and also found that benzaldehyde, benzene and carbon oxides were the main product of oxidation. However, they found a somewhat lower initial selectivity towards benzaldehyde (40% instead of 55%).

Furthermore, the reaction scheme proposed by Germain and Laugier may be incorrect as far as anthraquinone is concerned. The relatively large amount of anthraquinone formed by oxidation of benzaldehyde indicates that this is the major route for anthraquinone production.

### *Oxidation Kinetics*

The basis of the kinetic model is a redox mechanism with respect to the catalyst. Two reactions, oxidation of the catalyst by oxygen and reduction by an organic molecule, take place independently, even at different sites of the catalyst. Important evidence for independent reactions is given by Keulks (*28*) who demonstrated that oxygen originating from the catalyst is used in the first place, instead of oxygen adsorbed from the gas phase.

The oxidation of toluene, benzaldehyde and benzene by the catalyst was found to be first order in the reactant partial pressure. This is in good agreement with results of many others. As to the assumption of proportionality between oxidation rate and fraction of oxidized sites on the catalyst [(Eq. (3)], the investigations presented here cannot give experimental evidence. Observations of Matsuura and Schuit (*23*), however, may justify these assumptions. They found that the rate of combustion of butadiene to carbon oxides is proportional to the degree of oxidation of the catalyst at temperatures above 400°C. Hence it can be assumed proportional to the fraction of oxidized sites, because the rapid oxygen diffusion at this temperature level will establish an equilibrium between surface and bulk oxygen.

The reoxidation of the catalyst was found to be first order in the oxygen partial pressure. Again the results of Matsuura and Schuit (*23*) will be considered. They measured oxygen sorption rates for bismuth molybdates above 400°C and concluded the following: (a) the rate of sorption (reoxidation) is first order in the oxygen partial pressure; (b) the rate of sorption is proportional to the degree of reduction (and hence to the fraction of reduced sites on the surface); (c) the energy of activation for the sorption has the order of magnitude of 20 kcal/mole. The results of the toluene oxidation are in good agreement with points a and c, while the second statement is equivalent to the assumption of proportionality between $R_{O_2}$ and $(1 - \theta_{O_2})$ [(Eq. (5)].

So far the assumptions as to the kinetic model equations look reasonable. However, derivation of the rate equations originated from the idea that an active site for oxidation was related to an oxygen atom at the catalyst surface and that after oxidation the same site should be an active center for reoxidation of the catalyst. This is not necessarily true, the more so as different types of active sites may be present according to Matsuura and Schuit (*23,24*). However the kinetic model presented here might then be correct as well. It only demands redefinition of $\theta_{O_2}$ in the kinetic equations as the fraction of oxygen atoms in the catalyst bulk, and $1 - \theta_{O_2}$ as the number of bulk vacancies, both related to the maximum amount of oxygen that can participate in the reactions. In that case the assumptions with respect to the dependence of reaction rates on the oxidation state of the catalyst would correspond directly with the observations of Matsuura and Schuit (*23,24*) and the question of the nature of active sites is left open.

A peculiar result of the investigations presented here is the equality of activation energies for the three different oxidation steps. An analogous result is reported by Germain (*36*) for the oxidation of naphthalene over vanadium pentoxide, in which four oxidation reactions are involved. It is obvious to think of common rate determining steps with a common type of transition state for each of these oxidation reactions. In analogy with the mechanism proposed for the oxidation of propene over bismuth molybdate (*5,15,23,24,37*), one might think of a dissociative adsorption of the aromatic hydrocarbon (H-abstraction) followed by the forming of a transition state of the molecule bonded to a bismuth atom. If the aromatic nucleus determines the type of bonding similarity in aromatic oxidation reactions can be imagined. Detailed mechanistic theories, however, are beyond the scope of the present investigations.

## ACKNOWLEDGMENTS

The authors thank Messrs. J. J. Grootendorst, W. D. Both, J. M. Kooper and A. van Dongen, who performed most of the experimental work and contributed in many fruitful discussions. Thanks are due also to the Analysis Group for their valuable assistance.

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