# Kinetics of Selective Oxidation of Toluene and Methanol over Supported $V_2O_5$-Alkalimetal Sulfates

The catalytic activity of supported $V_2O_5$-alkalimetal sulfate catalysts was studied by oxidizing toluene and methanol to aldehydes and water. An isothermal, fixed-bed reactor, operating at atmospheric pressure and temperatures of 320, 345, and 370°C, was used to obtain the reaction rate data for different partial pressure combinations of the reaction components of these two systems. Three different approaches, Langmuir-Hinshelwood, Hinshelwood, and two-step redox mechanisms, have been used to study the kinetics, with statistical data interpretation.

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## SCOPE

Selective vapor-phase oxidation of hydrocarbons and alcohols, using air as the oxidizing agent, has attracted much attention in the last 20 years, as is obvious from the great number of articles published in this field. Relatively little attention has been given in the literature to study the kinetics of selective oxidation of analogous reactions on the same catalyst with the aim of proposing a common theory for all such similar reactions. Although physico-chemical insight and several formalisms limit the spectrum of possible models for a catalytic reaction, a detailed kinetic investigation of such reactions requires obtaining precise experimental data followed by model discrimination and parameter estimation.

The production of benzaldehyde from toluene and formaldehyde from methanol over supported $V_2O_5$-alkalimetal sulfate catalysts have been chosen as the model reactions for study of oxidation kinetics. The selective oxidation of toluene and methanol to aldehydes over supported $V_2O_5$-$K_2SO_4$ catalyst have only been reported by Downie, Shelstad, and Graydon (1961) and Agarwal, Nigam, and Srivastava (1978), respectively. However, due to lack of precise experimental data, these studies were not accompanied by any statistical testing of the results. In this kinetic investigation, increased emphasis has been placed on modelling and parameter estimation. It is hoped that the present work will lead to a plausible mechanism which may provide a link between toluene and methanol oxidation over supported $V_2O_5$-alkalimetal sulfate catalyst.

## CONCLUSIONS AND SIGNIFICANCE

Activity data are reported for the oxidation of toluene and methanol over a series of $V_2O_5$-alkalimetal sulfate catalysts. The additive activity series was $K_2SO_4 > Na_2SO_4 > Li_2SO_4$.

Kinetic data have been obtained for the oxidation of toluene and methanol over a silica supported $V_2O_5$-$K_2SO_4$ catalyst. A comparison of the oxidation results of toluene with that of methanol revealed a common reaction mechanism. The data have been correlated best by a rate equation developed on the basis of a two-step redox mechanism. In addition to statistical data interpretation, the resulting rate equation was based on insight into the true physico-chemical nature of the process.

It is expected that the present results will contribute to the understanding of the kinetics and mechanisms of such reactions.

## INTRODUCTION

Numerous investigations have been made on the kinetics of different oxidation reactions over $V_2O_5$ catalyst. In addition to some metal oxides, the addition of alkalimetal sulfates to vanadium pentoxide has been shown to influence its catalytic activity (Sharma, Rai, and Srivastava, 1980; Sharma and Srivastava, 1980; Agarwal, Nigam, and Srivastava, 1978; Krupay and Ross, 1977; Downie, Shelstad, and Graydon, 1961; Tandy, 1956). Although the kinetics of oxidation of some organic compounds over supported $V_2O_5$-alkalimetal sulfate catalysts have been reported, relatively little attention has been given to interpreting the results in a way providing a link between toluene and methanol oxidation on the same catalyst.

The only works reported on the kinetics of oxidation of toluene and methanol over $V_2O_5$-$K_2SO_4$ catalyst are those of Downie, Shelstad, and Graydon (1961) and Agarwal, Nigam, and Srivastava (1978), respectively. Downie et al. studied toluene oxidation and limited their analysis to a modified Hinshelwood model. No attempt at other mechanisms was made, since there was considerable scatter in their experimental data. On the other hand, Agarwal et al. (1978) carried out the oxidation of methanol at a high conversion level and considered only a two-step redox mechanism. The effect of different products on reaction rates was not investigated. Also, in both these investigations, no attempt on model discrimination and parameter estimation was made. Both tasks are evidently based on reliable experimental data.

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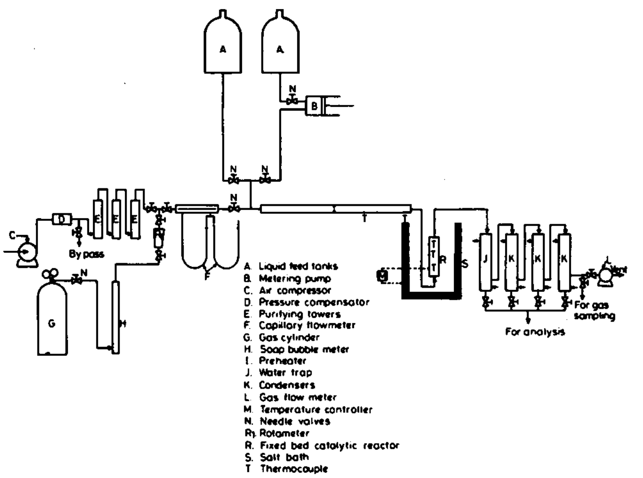

Figure 1. Equipment schematic.

Recently, Froment (1975) has discussed in detail the estimation of parameters and has emphasized the necessity of the statistical testing of the results. Kittrell et al. (1965) have shown that substantially different conclusions about the describing model and its parameter values can be drawn, depending on the type of analysis and data weighting chosen and have stressed the need for nonlinear least squares analysis of the catalytic rate models. Accuracy of the experimental data is no guarantee of a successful kinetic analysis when the experimental program suffers from a lack of insight into the effect of different variables and is poorly designed. Regression analysis can sometimes lead to substantially different conclusions about the describing model and its parameter values due to poor experimental design and lack of physico-chemical insight. The estimated parameter values may be strongly interdependent in some cases.

In this kinetic investigation, air oxidation of methanol and toluene were studied over a series of silica supported $V_2O_5$-alkalimetal sulfate catalysts at atmospheric pressure and temperatures of 320, 345, and 370°C. The experimental results are analyzed on the basis of Langmuir-Hinshelwood, modified Hinshelwood, and two-stage redox kinetics, with statistical data interpretation to show the real significance of mechanism determination with precise experimental data. An attempt has also been made to propose such a mechanism which would provide a link between toluene and methanol oxidation on the same catalyst.

## EXPERIMENTAL METHODS

### Preparation of the Catalyst

A series of $V_2O_5$ and lithium, sodium, and potassium sulfates supported on silica catalysts containing up to 70 wt. % active phase was prepared by the impregnation technique. The impregnate was vacuum-dried at 70°C and then calcined at 550°C for 6 h. The alkalimetal sulfate content in all the samples of the series, ranged from 10 to 20%. Reference to various samples will be made giving their composition as wt. % $V_2O_5$ and alkalimetal sulfate, $M_2SO_4$, where *M* represents lithium, sodium, or potassium. Hence, V-20-*M*-15 means a sample of $V_2O_5$-$M_2SO_4$ on silica having 20% of active component as $V_2O_5$, 15% of the promoter as alkalimetal sulfate, and the balance as silica.

### Apparatus and Procedure

Reactions were carried out in a fixed bed-type reactor with a continuous flow system at atmospheric pressure. The apparatus was similar to that used by Agarwal, Nigam, and Srivastava (1978) in the oxidation of methanol. However, some of the details of the equipment vary between experiments. A brief description of the equipment used in this study is necessary. A general schematic diagram of the experimental equipment is shown in Figure 1. Compressed air was passed through the drier and purifying towers containing fused calcium chloride, potassium hydroxide pellets, and active charcoal and metered through a flowmeter to the preheater. The organic feed was vaporized in 1.27 cm o.d. tube wrapped with insulating heating tape. These vapors were carried by an incoming airstream and the air-feed mixture was led to the reactor through a preheating section.

The reactor was stainless steel tubing (2.54 cm in diameter and 15.24 cm long) placed into the salt bath. A wire-mesh (−60 + 80 size) was welded at the bottom of the reactor for the catalyst support. Temperatures at various points in the reactor, including the catalyst bed and preheater were measured with the help of iron-constantan thermocouples. The thermocouples were calibrated against a 25 ohm Leeds and Northrup platinum resistance thermometer and Mueller bridge assembly. The average temperature was the mean of the temperatures measured at a point in the reactor at different time intervals, and was controlled to within 0.5°C of the desired value. The dilution of the catalyst with porcelain beads and the presence of large amount of inert nitrogen in the feed stream ensured the isothermal conditions in the reactor.

The experimental data were taken under steady-state conditions, in which a minimum of seven runs were made in 30-min. intervals after steady state has been attained. The average of the last two values of these analyses was used for the estimation of conversion. The standard deviation was less than 1.5%. In the case of methanol oxidation, the reaction products were passed through a water trap and ice water condensers. The lighter gaseous products, carbon dioxide, carbon monoxide, oxygen, and nitrogen were analyzed intermittently.

Fresh catalyst was used in each experiment. The activity of catalyst was practically constant during an experimental run. However, it has already been shown (Sharma, Rai, and Srivastava; 1980) that the activity of a spent catalyst used for 50 runs was about 15% less than that for a fresh catalyst.

### Analytical Techniques

The analyses for products of toluene oxidation were performed by employing a C.I.C.A.C. gas chromatograph, provided with a hydrogen flame detector, thermostated temperature control of oven and injector along with temperature programming facilities, and an output response recorder. The chromatographic column was a 2-m length of 3.2 mm stainless steel tubing containing 10% SE-30 on Chromosorb *W* (−80 + 100 size). The temperature of the injector was kept constant at 250°C and the oven temperature was programmed from 110 to 210°C at a rate of 5°C $\text{min}^{-1}$. Sample size of 0.4 $\mu$l was used.

The reaction products of methanol oxidation were also analyzed by the chromatographic method. The analyzing column was filled with Teflon supported on Carbowax 1500 and was 2.5 m long and 3.2 mm in diameter. The temperatures of the injector port, oven, and detector were 110, 80, and 110°C, respectively.

Carbon dioxide and water were analyzed by a Porapak *Q* chromatographic column, operated at 60°C, while oxygen, nitrogen, and carbon monoxide were determined on a column filled with molecular sieve.

## RESULTS

### Activity of Various Catalysts

The catalytic activities of a series of supported $V_2O_5$-alkalimetal sulfate catalysts for oxidation of toluene and methanol were examined. The catalytic activity was defined as the number of moles of aldehyde formed per mole of toluene or methanol fed. The reaction conditions were as follows: for toluene oxidation, temperature = 350°C, $\bar{R}$ = 1.63, $W/F$ = 82.5 g · $\text{mol}^{-1}$/h; for methanol oxidation, temperature = 350°C, $\bar{R}$ = 11, $W/F$ = 40 g · $\text{mol}^{-1}$/h. It is evident from Figure 2 that potassium-promoted catalysts have the higher activity than

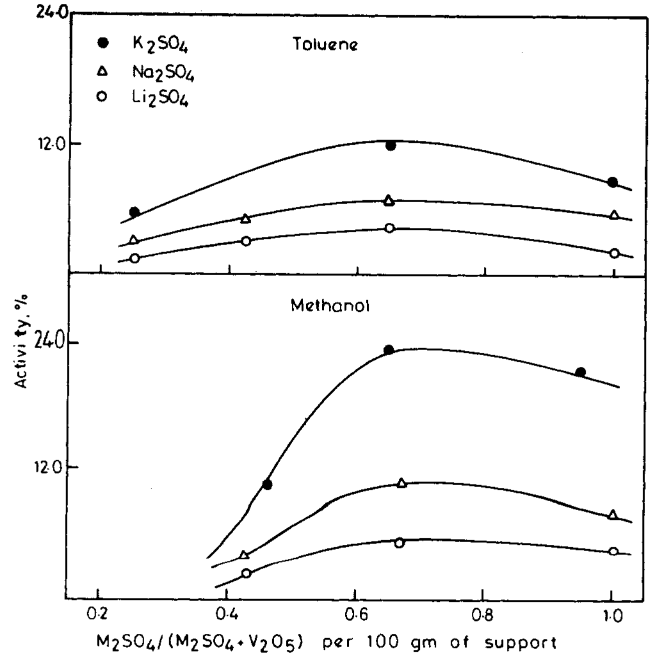

Figure 2. Effect of promoter concentration on activity.

those with lithium or sodium. The additive activity series is $Li_2SO_4 < Na_2SO_4 < K_2SO_4$. The same trend has been observed in the studies of the catalytic oxidation of sulfur dioxide (Tandy, 1956; Dzisyak et al., 1961; Bibin and Kasatkina, 1964). Also, the activity is highest at an alkalimetal sulfate to $V_2O_5$ weight ratio of about 0.65/100 g of support. This corresponded to a catalyst of composition 20% $V_2O_5$, 15% $K_2SO_4$, and balance as silica (V-20-K-15).

Since silica-supported $V_2O_5$-$K_2SO_4$ catalyst with composition 20% $V_2O_5$ and 15% $K_2SO_4$ was proved to be the best catalyst for both these oxidation reactions, all experiments described below were made exclusively with this catalyst. A detailed physico-chemical characterization by means of x-ray, d.t.a., t.g.a., electron microscopy, and B.E.T. studies for this system has been described elsewhere (Sharma, Rai, and Srivastava, 1980). The surface area, pore volume, and mean pore radius for this catalyst composition were 5.2 $m^2 g^{-1}$, 0.3030 $mL\, g^{-1}$ and 1165 Å, respectively, and the average particle size was about 1 $\mu m$. The average size of the catalyst granules was (−8 + 10) mesh size.

Preliminary runs with an empty reactor and a reactor filled with porcelain beads indicated that the homogeneous reaction and the catalytic action of the system were not important under the experimental conditions. The effects of diffusion were kept to a minimum by passing the gas at high velocity through the catalyst. The fair constancy of conversion obtained by changing the feed rate while keeping $(W/F)$ constant suggested that the diffusion of the gases was not controlling the rate. The role of internal diffusion was checked by varying the size of the catalyst particles while maintaining the catalyst weight, $\bar{R}$, and $(W/F)$ constant. The internal diffusion resistance in the catalyst particles was practically negligible as observed by the insignificant change in the reaction rate. To study the effect of external diffusion, it was necessary to increase the bed height while

TABLE 1. SUMMARY OF EXPERIMENTS

| No. of series | Feed Composition, mol % Toluene | Oxygen | Nitrogen | Space-time, g · h/gmol |
|---|---|---|---|---|
| *Toluene* | | | | |
| 5 | 2.90 | 20.40 | 76.70 | 15-35 |
| 5 | 4.76 | 20.00 | 75.24 | 15-35 |
| 5 | 6.55 | 19.60 | 73.85 | 15-35 |
| Total number of experiments, 45 | | | | |
| *Methanol* | | | | |
| 5 | 8.0 | 19.3 | 72.7 | 20-60 |
| 5 | 10.0 | 18.9 | 71.1 | 20-60 |
| 5 | 12.0 | 18.4 | 69.6 | 20-60 |
| Total number of experiments, 45 | | | | |

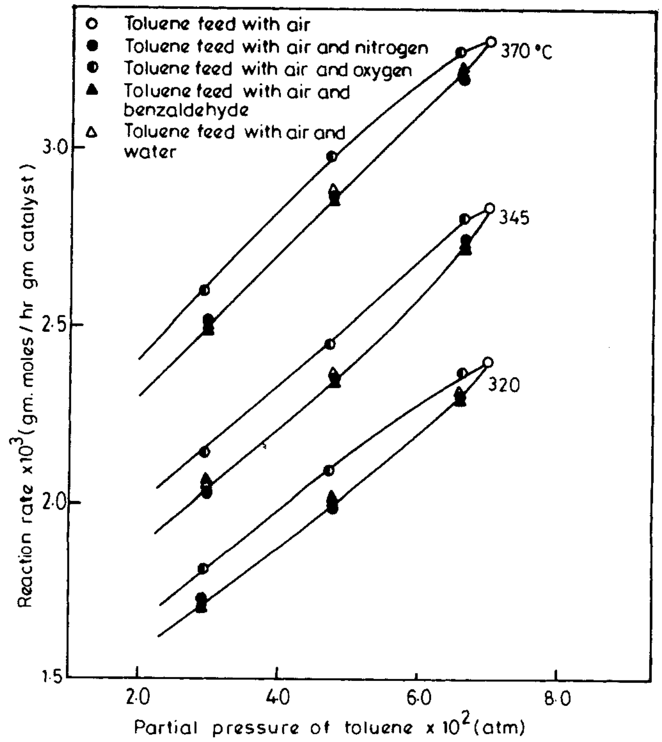

Figure 3. Partial rate data for toluene.

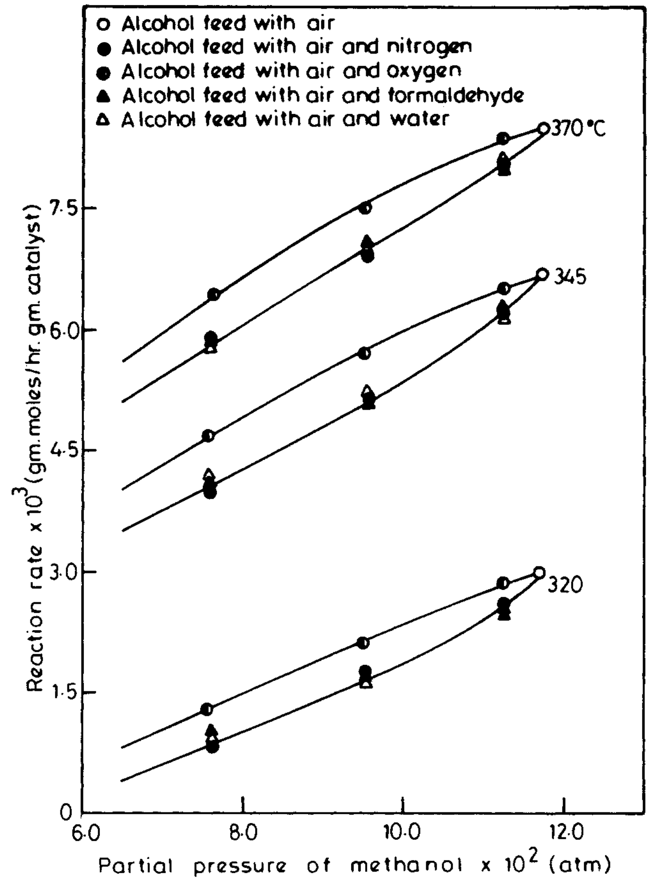

Figure 4. Partial rate data for methanol.

keeping ($\bar{R}$) and ($W/F$) constant. The rate was unaffected by doubling the bed height. Thus, the external diffusion in the catalyst bed was negligible. Rate calculations were based on conversion to benzaldehyde or formaldehyde.

The experimental conditions were so chosen by preliminary investigation that aldehyde was the only product of oxidation. No side reaction was taking place in the case of toluene. Methanol oxidation, however, did reveal the presence of carbon monoxide and carbon dioxide but were of negligible amount; they were not included in the kinetic analyses. Introductory experiments were also carried out with mixed feed to study product inhibition to obtain enough information for discrimination between possible kinetic schemes and models. The data points in which the reactor feed was a mixture of air, toluene or methanol, and one other component are in Figures 3 and 4. These graphs indicate that oxygen pressure influences the rates of both the reactions, however, adsorption of water and aldehyde have no appreciable effect on the reaction rate under the conditions studied. No attempt to determine the equilibrium adsorption constants of the products individually was made.

The effect of various variables, reactant mole ratio, $\bar{R}$; reaction temperature, T; the reciprocal space velocity, $W/F$, on the conversion were investigated. During the runs, different feed ratios were obtained by adjusting the air flow rate, while the reciprocal space velocity was varied by changing the amount of catalyst.

A large number of experiments were carried out to study the kinetics of the two systems. Table 1 gives the various compositions of feed at different space times for each isothermal set of runs. Data were collected at 320, 345, and 370°C. The feed rates for toluene and methanol were between 0.14 to 0.6 g · mol$^{-1}$/h. The measured reaction rate data are summarized in Tables A1 and A2, Appendix A. Because of large amount of inert (nitrogen) present in the feed stream, the pressures have been calculated up to five significant figures, though the pressures without including nitrogen were only known to three places.

## DISCUSSION OF RESULTS

The experimental data (Tables A1 and A2, Appendix A) have been analyzed according to the methods discussed in detail by Froment (1975). The techniques of linear and nonlinear estimates were applied to various mathematical rate expressions as a method of correlating the experimental data. Different models based on Langmuir-Hinshelwood mechanism were formulated using the approach suggested by Hougen and Watson (1947). In this method, various mechanisms which might control the reaction are postulated based on single site and two types of active sites. A Hinshelwood model (1949) was also derived, in which a steady-state concentration of oxygen is established on the catalyst surface and the rate of removal of oxygen by chemical reaction is equal to the rate of adsorption of oxygen. The kinetic rate expressions based on a two-stage redox mechanism, originally suggested by Mars and Van Krevelen (1954) for the vapor-phase oxidation of aromatic hydrocarbons on vanadium pentoxide, were derived assuming a steady state between reduction of the catalyst by organic compound and oxidation of the reduced catalyst by oxygen, which remains exclusively in the gas phase.

## MATHEMATICAL MODELLING AND DATA ANALYSIS

A nonlinear regression algorithm (Athappan and Srivastava, 1980; Goyal, Kudchadkar and Srivastava, 1978) utilizing Marquardt's algorithm (Marquardt, 1963; Draper and Smith, 1966) was used to obtain a mathematical fit for various rate expressions derived from Langmuir-Hinshelwood (Yang and Hougen, 1950), modified Hinshelwood, and redox mechanisms. The program minimized the residual sum of squares (R.S.S.) during the regression:

$$\text{R.S.S.} = \sum_{j=1}^{t} [r(j) - r(j)]^2$$

TABLE 2. MODELS REMAINING AFTER ISOTHERMAL REGRESSION

Reactions: $\underset{(A)}{C_6H_5CH_3} + \underset{(B)}{O_2} \rightarrow \underset{(R)}{C_6H_5CHO} + \underset{(W)}{H_2O}$

$\underset{(A)}{CH_3OH} + \underset{(B)}{½O_2} \rightarrow \underset{(R)}{HCHO} + \underset{(W)}{H_2O}$

Inert:Nitrogen (N)

| Model | Rate Controlling step | Rate equation | |
|---|---|---|---|
| | | Toluene | Methanol |
| | *Langmuir-Hinshelwood* | | |
| SA-2 | Single-site adsorption of A with B in the gas phase | $r = \dfrac{kp_A}{(1 + K_Rp_R)}$ | — |
| SB-2 | Single-site adsorption of B with A in the gas phase | $r = \dfrac{kp_B}{(1 + K_Rp_R)}$ | — |
| SSAOD-4 | Single-site surface reaction with A in the gas phase and oxygen dissociated (products not adsorbed) | $r = \dfrac{kK_Bp_Ap_B}{(1 + 1\sqrt{K_Bp_B})^2}$ | $r = \dfrac{kK_Bp_Ap_B}{(1 + 1\sqrt{K_Bp_B})^2}$ |
| DB-4 | Dual-site, adsorption of B | $r = \dfrac{kp_B}{(1 + K_Ap_A)}$ | — |
| DAOD-4 | Dual-site, adsorption of A with oxygen dissociated | — | $r = \dfrac{kp_A}{(1 + 1\sqrt{K_Bp_B})}$ |
| | *Modified Hinshelwood* | | |
| SSA-M | Rate of adsorption of oxygen = rate of chemical reaction | $r = \dfrac{kk_Bp_Ap_B}{(k_Bp_B + \alpha kp_A)}$ | $r = \dfrac{kk_Bp_Ap_B}{(k_Bp_B + \alpha kp_A)}$ |

TABLE 3. ISOTHERMAL REGRESSION—TOLUENE OXIDATION

*Langmuir-Hinshelwood*

| Model | Temp. (°C) | $k$ (g mol · h$^{-1}$ · g$^{-1}$ · atm$^{-1}$) | $K_A$ (atm$^{-1}$) | $K_B$ (atm$^{-1}$) | $K_R$ (atm$^{-1}$) | Avg. Abs. % Error | R.S.S. |
|---|---|---|---|---|---|---|---|
| SA-2 | 320 | (0.0688 ± 0.0030) | | | (560.1021 ± 57.0251) | 0.178 | $0.0029 \times 10^{-4}$ |
| | 345 | (0.0878 ± 0.0045) | | | (565.5521 ± 60.6400) | 0.258 | $0.0055 \times 10^{-4}$ |
| | 370 | (0.1231 ± 0.0046) | | | (636.4325 ± 43.1875) | 0.314 | $0.0041 \times 10^{-4}$ |
| SB-2 | 320 | (0.0079 ± 0.0018) | | | (143.8521 ± 178.8900) | 0.407 | $0.1084 \times 10^{-4}$ |
| | 345 | (0.0099 ± 0.0039) | | | (362.6254 ± 1.6235) | 0.098 | $0.2579 \times 10^{-4}$ |
| | 370 | (0.0122 ± 0.0051) | | | (342.2861 ± 2.7314) | 0.093 | $0.3878 \times 10^{-4}$ |
| SSAOD-4 | 320 | (0.0799 ± 0.0073) | | ( 125.9512 ± 97.6715) | | 0.095 | $0.1738 \times 10^{-4}$ |
| | 345 | (0.0961 ± 0.0132) | | (1487.2050 ± 2287.4467) | | 0.131 | $0.9079 \times 10^{-4}$ |
| | 370 | (0.1153 ± 0.0145) | | ( 972.1962 ± 632.1715) | | 0.054 | $1.1448 \times 10^{-4}$ |
| DB-4 | 320 | (0.0055 ± 0.0034) | ( 4.0529 ± 1.6569) | | | 0.085 | $0.2569 \times 10^{-4}$ |
| | 345 | (0.0067 ± 0.0001) | ( 8.9215 ± 5.8084) | | | 0.098 | $0.4530 \times 10^{-4}$ |
| | 370 | (0.0088 ± 0.0078) | (10.7617 ± 20.6260) | | | 0.095 | $6.4400 \times 10^{-4}$ |

*Modified Hinshelwood*

| Model | Temp. (°C) | $k$ (g · mol · h$^{-1}$ · g$^{-1}$ · atm$^{-1}$) | $k_B$ (g · mol · h$^{-1}$ · g$^{-1}$ · atm$^{-1}$) | Avg. Abs. % Error | R.S.S. |
|---|---|---|---|---|---|
| SSA-M | 320 | (0.0607 ± 0.0007) | (0.0011 ± 0.0041) | 0.494 | $0.1741 \times 10^{-4}$ |
| | 345 | (0.1430 ± 0.0098) | (0.0089 ± 0.0006) | 0.608 | $0.1707 \times 10^{-4}$ |
| | 370 | (0.5681 ± 0.0787) | (0.0153 ± 0.0012) | 0.653 | $0.0252 \times 10^{-4}$ |

The nonlinear computer program basically improved upon the initial estimates of various constants of the rate equation until the R.S.S. could no longer be reduced. Approximately 95% confidence intervals for various constants were calculated from estimates of their individual variances ($\sigma^2$). An estimate of the variances of each model was calculated from the R.S.S. and the appropriate degrees of freedom (DF). The various models were compared by forming a variance ratio. An $F$ test with the proper degrees of freedom was then used to determine, if the variances were significantly different at the 95% level. The starting values of the parameters of the various models were estimated by linear regression.

The mechanistic models were constructed with the implicit assumption that the underlying model parameters are independent and have some physico-chemical significance. The interdependence of the parameter values 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. This problem has been overcome by taking all experimental series (in which different conditions were varied one at a time) and by performing a single combined regression. The combination of all series was possible, since the catalyst activity was constant.

The two reactions studied are:

$$\underset{(A)}{C_6H_5CH_3} + \underset{(B)}{O_2} \rightarrow \underset{(R)}{C_6H_5CHO} + \underset{(W)}{H_2O} \qquad \underset{(N)}{\text{Inert:nitrogen}} \qquad (1)$$

$$\underset{(A)}{CH_3OH} + \underset{(B)}{\tfrac{1}{2}O_2} \rightarrow \underset{(R)}{HCHO} + \underset{(W)}{H_2O} \qquad \underset{(N)}{\text{Inert:nitrogen}} \qquad (2)$$

The thermodynamic calculations have shown that both reactions are essentially irreversible with the equilibrium constants of $2.5 \times 10^{57}$ and $3.4 \times 10^{31}$ (Sharma, 1980), at 25°C and 1 atm. pressure, for Eqs. 1 and 2, respectively. The method of Yang and Hougen (1950) was used to eliminate some of the rate-controlling steps. The rate data showed that desorption of product was not a rate-controlling step.

TABLE 4. ISOTHERMAL REGRESSION—METHANOL OXIDATION

*Langmuir-Hinshelwood*

| Model | Temp. (°C) | $k$ (g mol · h$^{-1}$ · g$^{-1}$ · atm$^{-1}$) | $K_B$ (atm$^{-1}$) | Avg. Abs. % Error | R.S.S. |
|---|---|---|---|---|---|
| SSAOD-4 | 320 | (0.0168 ± 0.0057) | (139.5301 ± 2775.0410) | 0.833 | $0.0743 \times 10^{-4}$ |
| | 345 | (0.1330 ± 0.0236) | ( 14.9860 ± 11.9080) | 0.285 | $0.2519 \times 10^{-4}$ |
| | 370 | (0.2414 ± 0.0377) | ( 8.7311 ± 2.3530) | 0.146 | $0.3568 \times 10^{-4}$ |
| DAOD-4 | 320 | (0.0919 ± 0.0226) | (135.4200 ± 6700.0000) | 3.776 | $0.3206 \times 10^{-4}$ |
| | 345 | (0.3498 ± 0.0315) | (130.5050 ± 288.7615) | 1.145 | $0.3372 \times 10^{-4}$ |
| | 370 | (0.0963 ± 0.0141) | ( 0.4712 ± 1.5721) | 0.600 | $0.3848 \times 10^{-4}$ |

*Modified Hinshelwood*

| Model | Temp. (°C) | $k$ (g mol · h$^{-1}$ · g$^{-1}$ · atm$^{-1}$) | $k_B$ (g mol · h$^{-1}$ · g$^{-1}$ · atm$^{-1}$) | Avg. Abs. % Error | R.S.S. |
|---|---|---|---|---|---|
| SSA-M | 320 | (0.0159 ± 0.0056) | (0.0091 ± 0.0061) | 0.247 | $0.0733 \times 10^{-4}$ |
| | 345 | (0.0625 ± 0.0134) | (0.0571 ± 0.0321) | 0.067 | $0.3080 \times 10^{-4}$ |
| | 370 | (0.0897 ± 0.0153) | (0.0922 ± 0.0058) | 0.064 | $0.3460 \times 10^{-4}$ |

TABLE 5. ISOTHERMAL REGRESSION—TWO-STAGE REDOX MODELS

| Model | Temp. (°C) | $k_1$ (g mol · h$^{-1}$ · g$^{-1}$ · atm$^{-m}$) | $k_2$ (g mol · h$^{-1}$ · g$^{-1}$ · atm$^{-n}$) | Avg. Abs. % Error | R.S.S. |
|---|---|---|---|---|---|
| | | | *Toluene* | | |
| VK-2 | 320 | (0.1056 ± 0.0159) | (0.0032 ± 0.0003) | 0.049 | $0.0045 \times 10^{-4}$ |
| | 345 | (0.1404 ± 0.0218) | (0.0036 ± 0.0003) | 0.0691 | $0.0087 \times 10^{-4}$ |
| | 370 | (0.1997 ± 0.0339) | (0.0040 ± 0.0003) | 0.063 | $0.0121 \times 10^{-4}$ |
| VK-3 | 320 | (0.0215 ± 0.0034) | (0.0156 ± 0.0021) | 0.462 | $0.0121 \times 10^{-4}$ |
| | 345 | (0.0135 ± 0.0011) | (0.0494 ± 0.0062) | 0.640 | $0.0091 \times 10^{-4}$ |
| | 370 | (0.1152 ± 0.0129) | (0.0148 ± 0.0017) | 0.475 | $0.0349 \times 10^{-4}$ |
| VK-4 | 320 | (0.0607 ± 0.0007) | (0.0011 ± 0.0041) | 0.494 | $0.1741 \times 10^{-4}$ |
| | 345 | (0.1430 ± 0.0098) | (0.0089 ± 0.0006) | 0.608 | $0.1707 \times 10^{-4}$ |
| | 370 | (0.5681 ± 0.0787) | (0.0153 ± 0.0012) | 0.653 | $0.0252 \times 10^{-4}$ |
| | | | *Methanol* | | |
| VK-4 | 320 | (0.0159 ± 0.0056) | (0.0091 ± 0.0061) | 0.247 | $0.0733 \times 10^{-4}$ |
| | 345 | (0.0625 ± 0.0134) | (0.0571 ± 0.0321) | 0.067 | $0.3080 \times 10^{-4}$ |
| | 370 | (0.0897 ± 0.0153) | (0.0922 ± 0.0058) | 0.064 | $0.3460 \times 10^{-4}$ |

**Langmuir-Hinshelwood and Hinshelwood Mechanism**

The possible Langmuir-Hinshelwood isothermal rate equations based on single- and dual-site mechanisms for the two reactions are presented in Table B1, Appendix B. These rate equations were derived with an adsorption term for each of the reaction components and diluent nitrogen. Linear and nonlinear regressions of the rate equations were made at each temperature. All possible combinations of the various adsorption terms were examined to allow for various negligible adsorption terms. The isothermal rate equations, basic types of which are given in Table B1, Appendix B, thus resulted in 46 different mathematical forms (for each system) which were confronted with the experimental data (Tables A1 and A2, Appendix A).

Rate expressions were eliminated from further considerations, when any of the converged adsorption equilibrium constants became negative. Models can also be rejected on the basis of improper trends of these constants with the temperature, when, in actuality, these adsorption equilibrium constants are positive or have negative temperature coefficients. Of course, physical mechanisms which have such properties as adsorption equilibrium constants with positive temperature coefficients are extremely rare. If the constants of a model are actually unacceptable, the model has generally been rejected (Kittrell et al. 1965).

Included in Table B1, Appendix B, is a rate model derived on the basis of a modified Hinshelwood mechanism (Downie et al., 1961). Linear and nonlinear regressions were also carried out at each temperature. The choice of the model is based on the requirement that the temperature coefficients for rate constant and specific rate of adsorption should be positive.

Table 2 gives the rate models with all positive constants which had to be retained statistically after isothermal regressions. The converged values of the parameters of these models by nonlinear estimation are presented in Tables 3 and 4 for toluene and methanol oxidation, respectively. The discrimination was based on the requirement that the kinetic and adsorption constants had to be positive. The models with the large confidence intervals (approximately 95%) for the various parameters have also been omitted, because they were meaningless.

The data for toluene oxidation were most satisfactorily correlated by model SSA-M, based on modified Hinshelwood mechanism. Although, this model has close values of RSS and confidence limits with the remaining models of this table, the choice was based on the requirement of the proper trend of the constants with the temperature.

The methanol oxidation data were also better described by the same model SSA-M. The least value of the average absolute percentage error was found in this case as compared to model SSAOD-4. The variation in the constants (Model DAOD-4) showed an improper trend with temperature and was therefore rejected.

**Two-Stage Redox Models**

Agarwal et al. (1978), Mann and Dosi (1973), and Bhattacharya et al. (1967) have suggested the interpretation of the results of methanol oxidation over $V_2O_5$-mixed catalysts to be based on a two-stage redox mechanism, similar to the one postulated by Mars and Van Krevelen (1954). Their scheme is adopted below to include the toluene oxidation. According to this mechanism, a steady state is assumed between the following two steps:

$$m\ A(g) + Cat - \mathrm{O} \xrightarrow{k_1} R(g) + W(g) + Cat^{\bullet} \tag{3}$$

$$n\ \mathrm{O_2}(g) + Cat^{\bullet} \xrightarrow{k_2} Cat - \mathrm{O} \tag{4}$$

When the rates of both processes (Eqs. 3 and 4) are equal, it is possible to derive an expression for the oxidation of toluene or methanol:

$$r = \frac{k_1 p_A^m}{(1 + \alpha k_1 p_A^m / k_2 p_{O_2}^n)}\ , \tag{5}$$

where $m$ and $n$ are the reaction order with respect to organic compound $A$ and oxygen, respectively, and $\alpha$ is the number of oxygen molecules required to oxidize one molecule of organic compound to aldehyde.

The isothermal models, as presented in Table B2, Appendix B, for $m$ and $n$ between 0 and 1, were applied to the experimental data (Tables A1 and A2, Appendix A). Table 5 gives the nonlinear estimates of the parameters of the rate models with all positive constants.

Model VK-4 ($m = 1$, $n = 1$) satisfactorily explains the kinetic data for methanol oxidation. For toluene oxidation, models VK-2 ($m = 1$, $n = 0$) and VK-4 ($m = 1$, $n = 1$) were found to describe the data more accurately. However, based on the sequential experimentation procedures, model VK-2 has been

TABLE 6. REGRESSION WITH TEMPERATURE

| Parameter | Estimate: Toluene | Estimate: Methanol |
|---|---|---|
| $k_1°$ | $1.5 \times 10^{11}$ | $9.5 \times 10^{7}$ |
| $\Delta E_1$ | 33.6 | 26.2 |
| $k_2°$ | $1.4 \times 10^{12}$ | $1.3 \times 10^{11}$ |
| $\Delta E_2$ | 40.6 | 35.3 |

rejected, since partial pressure of oxygen has been shown to influence the rate of reaction, Figure 3. Model VK-3 showed an improper trend with the temperature and, therefore, was not considered.

## COMPARISON BETWEEN TWO RIVAL MECHANISMS

Upon applying the criteria established in the preceding sections, it was evident that the oxidation process is not well described by any of the kinetic equations developed using Langmuir-Hinshelwood mechanism. However, modified Hinshelwood expression (model (SSA-M)) satisfactorily described the kinetics for both systems. Among the two-step redox models tested, the data for both toluene and methanol oxidations were satisfactorily correlated by model VK-4. Although both these mechanisms resulted in an identical rate expression, the significance of the parameters of the two models is different. Therefore, from a purely statistical point of view, it is impossible to say that one of these models describes the data best. The discrimination between these two rival mechanisms must be based on the physico-chemical insight and other experimental evidences.

The redox mechanism proposes the removal of actual lattice oxygen atoms by direct interaction with the reductant, which must hence be chemisorbed, while Hinshelwood mechanism ignores such a catalyst-reductant interaction and instead, suggests that only adsorbed oxygen molecules or atoms (and not the lattice oxygen) are removed by reacting with the reductant molecules, which remain exclusively in the gas phase.

The Hinshelwood model SSA-M was derived on the basis of an assumption that the rate of adsorption of oxygen is very small and a steady state is established in which rate of removal of oxygen by chemical reaction is equal to the rate of adsorption of oxygen. According to this interpretation, the specific rate of adsorption of oxygen should be independent of the organic compound oxidized when the same catalyst is used. Since the same catalyst composition was used in the present work for both toluene and methanol oxidations, a comparison can be made between the estimates of the specific rates of adsorption ($k_B$) for both reactions. In contrast, at all temperatures, the results indicate different values of $k_B$, Tables 3 and 4, for the two systems; the values differed by an approximate factor of 10.

It has been observed in the present studies that the color of the catalyst became black (characteristic of lower oxides of vanadium), when only toluene or methanol was allowed to pass over it for a short time. It was proved that the black color was not due to carbon deposition because carbon dioxide could not be detected in the exit gas of the regenerating cycle. The removal of lattice oxygen from $V_2O_5$ during the oxidation of organic compounds has also been suggested by various workers (Jiru et al., 1965, 1966; Berets and Clark, 1956; Simard et al., 1953; Bhattacharya et al., 1967).

Among three types of mechanisms, Langmuir-Hinshelwood, modified Hinshelwood, and two-step redox models, the latter has been chosen. The effect of temperature on the rate expression (model VK-4) was introduced by substituting the Arrhenius temperature dependency relation for each of the constants:

$$k = k^{\circ}\, e^{-\Delta E/RT}$$

The converged values of the parameters of this expression are given in Table 6. The values of the activation energies for the two constants are positive indicating a satisfactory temperature relationship.

## APPENDIX-A

TABLE A1. SUMMARY OF RATE DATA—TOLUENE

| Run Number | Average Partial Pressure, (atm) Oxygen | Toluene × 10 | Benzaldehyde × 10 | Water × 10 | Nitrogen | Average Reaction Rate × $10^3$ (g mol · $h^{-1}$ · $g^{-1}$) |
|---|---|---|---|---|---|---|
| | | | *Average Temperature = 320°C* | | | |
| 1 | 0.2035 | 0.2875 | 0.0036 | 0.0036 | 0.7669 | 1.86 |
| 2 | 0.2034 | 0.2860 | 0.0050 | 0.0050 | 0.7669 | 1.72 |
| 3 | 0.2033 | 0.2852 | 0.0058 | 0.0058 | 0.7669 | 1.60 |
| 4 | 0.2032 | 0.2843 | 0.0067 | 0.0067 | 0.7669 | 1.55 |
| 5 | 0.2031 | 0.2836 | 0.0075 | 0.0075 | 0.7669 | 1.47 |
| 6 | 0.1992 | 0.4686 | 0.0075 | 0.0075 | 0.7523 | 2.10 |
| 7 | 0.1990 | 0.4665 | 0.0094 | 0.0094 | 0.7523 | 1.97 |
| 8 | 0.1988 | 0.4650 | 0.0111 | 0.0111 | 0.7523 | 1.86 |
| 9 | 0.1987 | 0.4631 | 0.0129 | 0.0129 | 0.7523 | 1.81 |
| 10 | 0.1985 | 0.4616 | 0.0144 | 0.0144 | 0.7523 | 1.72 |
| 11 | 0.1950 | 0.6418 | 0.0122 | 0.0122 | 0.7383 | 2.50 |
| 12 | 0.1947 | 0.6388 | 0.0152 | 0.0152 | 0.7383 | 2.32 |
| 13 | 0.1944 | 0.6359 | 0.0181 | 0.0181 | 0.7383 | 2.22 |
| 14 | 0.1942 | 0.6335 | 0.0206 | 0.0206 | 0.7383 | 2.10 |
| 15 | 0.1939 | 0.6308 | 0.0232 | 0.0232 | 0.7383 | 2.02 |
| | | | *Average Temperature = 345°C* | | | |
| 16 | 0.2034 | 0.2864 | 0.0046 | 0.0046 | 0.7669 | 2.14 |
| 17 | 0.2033 | 0.2851 | 0.0060 | 0.0060 | 0.7669 | 2.06 |
| 18 | 0.2032 | 0.2840 | 0.0070 | 0.0070 | 0.7669 | 1.94 |
| 19 | 0.2031 | 0.2830 | 0.0080 | 0.0080 | 0.7669 | 1.85 |
| 20 | 0.2030 | 0.2821 | 0.0089 | 0.0089 | 0.7669 | 1.75 |
| 21 | 0.1991 | 0.4674 | 0.0087 | 0.0087 | 0.7523 | 2.43 |
| 22 | 0.1989 | 0.4651 | 0.0109 | 0.0109 | 0.7523 | 2.30 |
| 23 | 0.1986 | 0.4627 | 0.0133 | 0.0133 | 0.7523 | 2.24 |
| 24 | 0.1985 | 0.4610 | 0.0150 | 0.0150 | 0.7523 | 2.10 |
| 25 | 0.1983 | 0.4594 | 0.0166 | 0.0166 | 0.7523 | 2.00 |
| 26 | 0.1948 | 0.6395 | 0.0145 | 0.0145 | 0.7383 | 2.97 |
| 27 | 0.1944 | 0.6359 | 0.0181 | 0.0181 | 0.7383 | 2.77 |
| 28 | 0.1941 | 0.6326 | 0.0214 | 0.0214 | 0.7383 | 2.62 |
| 29 | 0.1938 | 0.6298 | 0.0242 | 0.0242 | 0.7383 | 2.46 |
| 30 | 0.1936 | 0.6275 | 0.0265 | 0.0265 | 0.7383 | 2.31 |

(Continued on following page)

*(Table A1. Continued from previous page)*

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | *Average Temperature = 370°C* | | | |
| 31 | 0.2033 | 0.2855 | 0.0056 | 0.0056 | 0.7669 | 2.56 |
| 32 | 0.2031 | 0.2838 | 0.0073 | 0.0073 | 0.7669 | 2.50 |
| 33 | 0.2030 | 0.2824 | 0.0087 | 0.0087 | 0.7669 | 2.40 |
| 34 | 0.2028 | 0.2812 | 0.0098 | 0.0098 | 0.7669 | 2.25 |
| 35 | 0.2028 | 0.2802 | 0.0108 | 0.0108 | 0.7669 | 2.12 |
| 36 | 0.1988 | 0.4546 | 0.0114 | 0.0114 | 0.7523 | 3.21 |
| 37 | 0.1986 | 0.4621 | 0.0139 | 0.0139 | 0.7523 | 2.92 |
| 38 | 0.1983 | 0.4596 | 0.0164 | 0.0164 | 0.7523 | 2.76 |
| 39 | 0.1981 | 0.4575 | 0.0185 | 0.0185 | 0.7523 | 2.60 |
| 40 | 0.1979 | 0.4554 | 0.0206 | 0.0206 | 0.7523 | 2.47 |
| 41 | 0.1944 | 0.6372 | 0.0168 | 0.0168 | 0.7383 | 2.43 |
| 42 | 0.1941 | 0.6329 | 0.0211 | 0.0211 | 0.7383 | 3.22 |
| 43 | 0.1937 | 0.6290 | 0.0250 | 0.0250 | 0.7383 | 3.06 |
| 44 | 0.1934 | 0.6256 | 0.0284 | 0.0284 | 0.7383 | 2.90 |
| 45 | 0.1931 | 0.6231 | 0.0309 | 0.0309 | 0.7383 | 2.70 |

TABLE A2. SUMMARY OF RATE DATA—METHANOL

| Run Number | Average Partial Pressure, (atm) | | | | | Average Reaction Rate × $10^3$ ($g\ mol \cdot h^{-1} \cdot g^{-1}$) |
|---|---|---|---|---|---|---|
| | Oxygen | Methanol × 10 | Formaldehyde × 10 | Water × 10 | Nitrogen | |
| | | | *Average Temperature = 320°C* | | | |
| 1 | 0.1930 | 0.7615 | 0.0367 | 0.0369 | 0.7256 | 1.75 |
| 2 | 0.1919 | 0.7612 | 0.0368 | 0.0377 | 0.7255 | 0.62 |
| 3 | 0.1909 | 0.7596 | 0.0380 | 0.0382 | 0.7254 | 0.60 |
| 4 | 0.1907 | 0.7581 | 0.0402 | 0.0410 | 0.7253 | 0.58 |
| 5 | 0.1906 | 0.7579 | 0.0404 | 0.0414 | 0.7252 | 0.57 |
| 6 | 0.1862 | 0.9516 | 0.0459 | 0.0462 | 0.7093 | 2.13 |
| 7 | 0.1859 | 0.9461 | 0.0512 | 0.0517 | 0.7092 | 1.40 |
| 8 | 0.1857 | 0.9441 | 0.0532 | 0.0540 | 0.7091 | 0.75 |
| 9 | 0.1856 | 0.9416 | 0.0545 | 0.0547 | 0.7090 | 0.45 |
| 10 | 0.1855 | 0.9404 | 0.0578 | 0.0579 | 0.7089 | 0.42 |
| 11 | 0.1835 | 1.1660 | 0.0664 | 0.0672 | 0.6940 | 2.41 |
| 12 | 0.1825 | 1.1251 | 0.0705 | 0.0718 | 0.6927 | 1.62 |
| 13 | 0.1802 | 1.1231 | 0.0875 | 0.0896 | 0.6919 | 1.55 |
| 14 | 0.1798 | 1.1152 | 0.0890 | 0.0920 | 0.6910 | 1.54 |
| 15 | 0.1785 | 1.0921 | 0.1016 | 0.1046 | 0.6902 | 1.46 |
| | | | *Average Temperature = 345°C* | | | |
| 16 | 0.1922 | 0.7516 | 0.0435 | 0.0444 | 0.7257 | 4.58 |
| 17 | 0.1902 | 0.7495 | 0.0478 | 0.0490 | 0.7250 | 4.08 |
| 18 | 0.1891 | 0.7230 | 0.0725 | 0.0745 | 0.7237 | 3.90 |
| 19 | 0.1877 | 0.7071 | 0.0878 | 0.0907 | 0.7236 | 2.53 |
| 20 | 0.1875 | 0.7043 | 0.0897 | 0.0933 | 0.7235 | 1.28 |
| 21 | 0.1856 | 0.9417 | 0.0549 | 0.0562 | 0.7091 | 5.58 |
| 22 | 0.1847 | 0.9262 | 0.0692 | 0.0713 | 0.7084 | 5.50 |
| 23 | 0.1845 | 0.9038 | 0.1255 | 0.1301 | 0.7071 | 4.68 |
| 24 | 0.1817 | 0.8589 | 0.1325 | 0.1369 | 0.7061 | 3.51 |
| 25 | 0.1806 | 0.8185 | 0.1440 | 0.1519 | 0.7034 | 2.77 |
| 26 | 0.1800 | 1.1170 | 0.0765 | 0.0805 | 0.6924 | 6.36 |
| 27 | 0.1781 | 1.0854 | 0.1005 | 0.1110 | 0.6914 | 6.28 |
| 28 | 0.1758 | 1.0464 | 0.1406 | 0.1491 | 0.6901 | 6.28 |
| 29 | 0.1722 | 0.9913 | 0.1901 | 0.2044 | 0.6884 | 6.04 |
| 30 | 0.1710 | 0.9542 | 0.1979 | 0.2561 | 0.6820 | 5.10 |
| | | | *Average Temperature = 370°C* | | | |
| 31 | 0.1923 | 0.7378 | 0.0562 | 0.0583 | 0.7253 | 6.25 |
| 32 | 0.1887 | 0.7246 | 0.0704 | 0.0743 | 0.7241 | 5.75 |
| 33 | 0.1873 | 0.7021 | 0.0915 | 0.0966 | 0.7233 | 5.70 |
| 34 | 0.1854 | 0.6782 | 0.1084 | 0.1254 | 0.7224 | 5.66 |
| 35 | 0.1836 | 0.6473 | 0.1379 | 0.1552 | 0.7213 | 5.62 |
| 36 | 0.1837 | 0.9008 | 0.0828 | 0.0866 | 0.7079 | 7.25 |
| 37 | 0.1818 | 0.8794 | 0.1103 | 0.1189 | 0.7068 | 7.00 |
| 38 | 0.1807 | 0.8390 | 0.1372 | 0.1666 | 0.6989 | 6.66 |
| 39 | 0.1771 | 0.8065 | 0.1738 | 0.1943 | 0.7043 | 6.56 |
| 40 | 0.1748 | 0.7727 | 0.2015 | 0.2306 | 0.7031 | 6.25 |
| 41 | 0.1754 | 1.0448 | 0.1324 | 0.1537 | 0.6900 | 9.50 |
| 42 | 0.1726 | 0.9954 | 0.1848 | 0.2007 | 0.6884 | 6.92 |
| 43 | 0.1704 | 0.9591 | 0.2163 | 0.2374 | 0.6872 | 5.66 |
| 44 | 0.1684 | 0.9302 | 0.2399 | 0.2686 | 0.6862 | 4.57 |
| 45 | 0.1667 | 0.9061 | 0.2581 | 0.2957 | 0.6853 | 3.75 |

# APPENDIX-B

## TABLE B1. POSSIBLE ISOTHERMAL RATE EQUATIONS

Reactions: $\underset{(A)}{C_6H_5CH_3} + \underset{(B)}{O_2} \rightarrow \underset{(R)}{C_6H_5CHO} + \underset{(W)}{H_2O}$ Inert:Nitrogen (N)

$\underset{(A)}{CH_3OH} + \underset{(B)}{\tfrac{1}{2}O_2} \rightarrow \underset{(R)}{HCHO} + \underset{(W)}{H_2O}$

*Langmuir-Hinshelwood*

A. Single-site Mechanism

1. *Oxygen Molecularly Adsorbed*

| Model | Rate Controlling Step | Rate Equation |
|---|---|---|
| SA | Adsorption of *A* (*B* in the gas phase) | $r = \dfrac{k(p_A - p_R p_W/Kp_B)}{\left(1 + \dfrac{K_A}{K} \cdot \dfrac{p_R p_W}{P_B} + K_R p_R + K_W p_W + K_N p_N\right)}$ |
| SB | Adsorption of *B* (*A* in the gas phase) | $r = \dfrac{k(p_B - p_R \cdot p_W/K \cdot p_A)}{\left(1 + \dfrac{K_B}{K} \cdot \dfrac{p_R p_W}{p_A} + K_R p_R + K_W p_W + K_W p_W\right)}$ |
| SSA | Surface reaction (*A* in the gas phase) | $r = \dfrac{kK_B(p_A p_B - p_R p_W/K)}{(1 + K_B p_B + K_R p_R + K_W p_W + K_N p_N)}$ |
| SSB | Surface reaction (*B* in the gas phase) | $r = \dfrac{kK_A(p_A p_B - p_R p_W/K)}{(1 + K_A p_A + K_R p_R + K_W p_W + K_N p_N)}$ |

2. *Oxygen Atomically Adsorbed*

| Model | Rate Controlling Step | Rate Equation |
|---|---|---|
| SBOD | Adsorption of *B* (*A* in the gas phase) | $r = \dfrac{k(p_B - p_R p_W/Kp_A)}{\left(1 + \dfrac{K_B}{K} \cdot \dfrac{p_R p_W}{p_A} + K_R p_R + K_W p_W + K_N p_N\right)^2}$ |
| SSAOD | Surface reaction (*A* in the gas phase) | $r = \dfrac{kK_B(p_A p_B - p_R p_W/K)}{(1 + \sqrt{K_B p_B} + K_R p_R + K_W p_W + K_N p_N)^2}$ |

B. Dual-site Mechanism

1. *Oxygen Molecularly Adsorbed*

| Model | Rate Controlling Step | Rate Equation |
|---|---|---|
| DA | Adsorption of *A* | $r = \dfrac{k(p_A - p_R p_W/Kp_B)}{\left(1 + \dfrac{K_A}{K} \cdot \dfrac{p_R p_W}{p_B} + K_B p_B + K_R p_R + K_W p_W + K_N p_N\right)}$ |
| DB | Adsorption of *B* | $r = \dfrac{k(p_B - p_R p_W/Kp_A)}{\left(1 + K_A p_A + \dfrac{K_B}{K} \cdot \dfrac{p_R p_W}{p_A} + K_R p_R + K_W p_W + K_N p_N\right)}$ |
| DS | Surface reaction | $r = \dfrac{kK_A K_B(p_A p_B - p_R p_W/K)}{(1 + K_A p_A + K_B p_B + K_R p_R + K_W p_W + K_N p_N)^2}$ |

2. *Oxygen Atomically Adsorbed*

| Model | Rate Controlling Step | Rate Equation |
|---|---|---|
| DAOD | Adsorption of *A* | $r = \dfrac{k(p_A - p_R p_W/K\sqrt{p_B})}{\left(1 + \dfrac{K_A}{K} \cdot \dfrac{p_R p_W}{\sqrt{p_B}} + \sqrt{K_B p_B} + K_R p_R + K_W p_W + K_N p_N\right)}$ |
| DBOD | Adsorption of *B* | $r = \dfrac{k(p_B - p_R p_W/Kp_A)}{\left(1 + K_A p_A + \dfrac{K_B}{K} \cdot \dfrac{p_R p_W}{p_A} + K_R p_R + K_W p_W + K_N p_N\right)^2}$ |
| DSOD | Surface reaction | $r = \dfrac{kK_A K_B(p_A p_B - p_R p_W/K)}{(1 + K_A p_A + \sqrt{K_B p_B} + K_R p_R + K_W p_W + K_N p_N)^3}$ |

*Modified Hinshelwood*

| Model | Rate Controlling Step | Rate Equation |
|---|---|---|
| SSA-M | rate of adsorption of *B* = rate of reaction (*A*, *R*, *W* and *N* in the gas phase) | $r = \dfrac{kk_B p_A p_B}{\alpha k p_A + k_B p_B}$ |

### TABLE B2. TWO-STAGE REDOX MODELS

Reactions: $\underset{(A)}{C_6H_5CH_3} + \underset{(B)}{O_2} \rightarrow \underset{(R)}{C_6H_5CHO} + \underset{(W)}{H_2O}$ Inert:Nitrogen (N)

$\underset{(A)}{CH_3OH} + \underset{(B)}{\tfrac{1}{2}O_2} \rightarrow \underset{(R)}{HCHO} + \underset{(W)}{H_2O}$

| Model | Reaction Order<br>$m$<br>(A) | <br>$n$<br>(B) | Rate Equation |
|---|---|---|---|
| VK-1 | 1 | 0.5 | $r = \dfrac{k_1p_A}{\left(1 + \dfrac{\alpha k_1 p_A}{k_2 p_B^{0.5}}\right)}$ |
| VK-2 | 1 | 0 | $r = \dfrac{k_1p_A}{\left(1 + \dfrac{\alpha k_1 p_A}{k_2}\right)}$ |
| VK-3 | 0.5 | 0 | $r = \dfrac{k_1p_A^{0.5}}{\left(1 + \dfrac{\alpha k_1 p_A^{0.5}}{k_2}\right)}$ |
| VK-4 | 1 | 1 | $r = \dfrac{k_1p_A}{\left(1 + \dfrac{\alpha k_1 p_A}{k_2 p_B}\right)}$ |
| VK-5 | 0.5 | 0.5 | $r = \dfrac{k_1p_A^{0.5}}{\left(1 + \dfrac{\alpha k_1 p_A^{0.5}}{k_2 p_B^{0.5}}\right)}$ |

## NOTATION

*Cat*-O = catalyst in oxidized form
$Cat^{\bullet}$ = catalyst in reduced form
$F$ = molar feed rate
$g$ = molecules in gas phase
$k$ = rate constant, g · mol/(h) (g) (atm)
$k_1$ = rate constant of oxidation of organic compound by oxygen from catalyst $Cat - O$, g · mol/(h) (g) (atm$^m$); (Table B2, Appendix B)
$k_2$ = rate constant of oxidation of catalyst $Cat^{\bullet}$ by oxygen, g · mol/(h) (g) (atm$^n$); (Table B2, Appendix B)
$k_B$ = specific rate of adsorption of oxygen, g · mol/(h) (g) (atm); (Table B1, Appendix B, model SSA-M)
$K_i$ = adsorption equilibrium constant of component $i$, (atm$^{-1}$); (Table B1, Appendix B, Langmuir-Hinshelwood models)
$K$ = thermodynamic equilibrium constant
$k^{\circ}$ = frequency factor, g · mol/(h) (g) (atm)
$M$ = represents K, Na or Li
$m$ = reaction order with respect to organic compound; (Table B2)
$n$ = reaction order with respect to oxygen; (Table B2)
$p_i$ = partial pressure of component $i$, (atm)
$R$ = mol % of organic compound (toluene or methanol) in the feed
$R$ = gas constant, (kcal)/(g · mol) (°K)
$r$ = experimental reaction rate, g · mol/(h) (g)
$\hat{r}$ = calculated reaction rate, g · mol/(h) (g)
$T$ = absolute temperature, °K
$W$ = weight of catalyst, g
$t$ = total number of data points
$\Delta E_1$ = activation energy for rate constant $k_1$, (kcal)/g · mol
$\Delta E_2$ = activation energy for rate constant $k_2$, (kcal)/g · mol
$\alpha$ = number of oxygen molecules required for converting one molecule of toluene or methanol to aldehyde
$\sigma^2$ = error variance

### Subscripts

$A$ = organic compound (methanol or toluene)
$B$ = oxygen
$N$ = nitrogen
$R$ = aldehyde
$W$ = water

### Definitions

$$\text{R.S.S.} = \sum_{j=1}^{t} [\hat{r}(j) - r(j)]^2$$

$$\sigma^2 = \sum_{j=1}^{t} [\hat{r}(j) - r(j)]^2/DF$$

$$\text{Avg. Abs. \% Error} = \frac{1}{t}\sum_{j=1}^{t}\left(\frac{\hat{r}(j) - r(j)}{r(j)}\right)(100)$$

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# Distribution Equilibrium Between a Bulk Phase and Small Pores

**The pore-bulk distribution coefficient $K$ for a solute species is calculated by modelling the solute molecules as hard spheres. $K$ is expanded in a virial-type series in powers of the bulk-phase concentration. The leading term is the Henry's law constant. The next two coefficients are reported for three pore shapes.**

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## SCOPE

**The phase equilibrium between pore and bulk solutions is relevant to several separation processes, such as adsorption, exclusion (gel-permeation) chromatography, and membrane transport. Of particular interest is the case of micropores, i.e. of pores whose characteristic linear dimension is within one order of magnitude of the size of the solute molecules. In many cases, the equilibrium between pore and bulk phases is dominated by an adsorptive (attractive) or a repulsive field exerted by the walls of the pore. Even in the absence of any such field, a partition process occurs due to the finite size of the solute molecules, which creates an exclusive region adjacent to the pore walls. All of these effects result from the interaction of single, isolated molecules with the pore walls, and are well understood. They correspond to the Henry's law regime, of proportionality between the concentrations in the bulk and in the pore. The present paper deals with the solute-solute interactions within the pore, which are important at all but the lowest concentrations, although they have been ignored to date. Because of these interactions, the distribution coefficient becomes concentration-dependent. Our goal has been to elucidate the nature of this dependence for micropores of three different shapes: a flat slit, an infinitely long circular cylinder and a spherical cavity.**

## CONCLUSIONS AND SIGNIFICANCE

**The pore-bulk distribution coefficient for a single solute whose molecules are modeled as hard elastic spheres can be expressed as a series in powers of the bulk concentration, Eq. 29 in this work. The leading term of this expansion is the Henry's law constant, and corresponds to the well-known steric exclusion effect due to the finite size of the molecules. The next two coefficients in the series were calculated. The calculation was done analytically for the case when the pore is shaped as a flat slit, and numerically for cylindrical and spherical pores. These coefficients are the most important results of the present research, and are shown as Eq. 34 and 35 and in Tables 2 and 3.**

**Often the distribution coefficients determined experimentally are found to be larger than the simple steric-exclusion value, and the difference is generally explained in terms of attractive forces (adsorption) due to the pore walls, or to changes in molecular configurations. The results reported here, which apply to pores with hard, nonadsorbing walls, introduce the effect of solute-solute interactions within the pores. They can be used to discriminate whether adsorption indeed exists, and to decide on its importance.**

## INTRODUCTION

This work deals with the properties of pure fluids and of molecular and colloidal solutions contained inside micropores, i.e. pores whose characteristic linear dimensions are comparable to the size of the fluid molecules (in the case of pure fluids) or to the size of the solute molecules or particles (in the case of solutions). The partition or distribution equilibrium between the pore and bulk phases is extremely relevant to various adsorption processes, to exclusion (gel permeation) chromatography, and to membrane transport and separations. The problems of the distribution of a pure fluid and of a single solute in solution can be described by formally identical equations, as we shall see below. The results presented here, however, are based on the properties of hard spheres and are thus of much greater relevance to the case of nonelectrolytic solutes. Consequently, we shall favor the language of solutions and refer to the distribution of solute molecules or particles.

The distribution coefficient is defined as the ratio of the average concentration inside the pore to the concentration of the bulk phase in equilibrium with it. The average intrapore concentration, however, is not a uniquely defined quantity, since it

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