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Catalytic Vapor-Phase Oxidation of p-Xylene Over Tin Vanadate

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Rates of oxidation of *p*-xylene were measured in the temperature range 320 to 420°C using tin vanadate as catalyst in an isothermal differential flow reactor. The amounts of *p*-xylene converted were determined by analyzing the main products (*p*-tolualdehyde, maleic anhydride, *p*-toluic acid and traces of terephthalic acid). Negligible amounts of products of complete combustion were formed.

The reaction rates obtained for *p*-xylene followed the relation,

$$\frac{k_X k_O C_X C_O}{k_O C_O + N k_X C_X},$$

based on the redox model.

The mechanism of the reaction was determined by conducting different sets of experiments and it was found that the reaction followed the parallel-consecutive mechanism, in which *p*-tolualdehyde and maleic anhydride were formed from the parallel route whereas *p*-toluic acid was formed from the consecutive route.

NOMENCLATURE

A	Frequency factor (liter g^{-1} catalyst sec^{-1})
C	Concentration (g moles $liter^{-1}$)
E	Energy of activation (kcal g $mole^{-1}$)
F	Feed rate (moles sec^{-1})
k_O	Adsorption rate constant of oxygen (liter g^{-1} catalyst sec^{-1})
k_X	Reaction rate constant of *p*-xylene (liter g^{-1} catalyst sec^{-1})
k	Reaction rate constant (g moles hr^{-1} g^{-1} catalyst)
N	Moles of oxygen consumed per mole of *p*-xylene converted
r_X	Reaction rate (moles g^{-1} catalyst sec^{-1})
T	Temperature in absolute scale
W	Weight of catalyst (g)
X	Conversion

Subscripts

O	Oxygen
X	*p*-Xylene
T	*p*-Tolualdehyde
M	Maleic anhydride
T′	*p*-Toluic acid
t	Total conversion or concentration

INTRODUCTION

The liquid-phase oxidation of *p*-xylene has been studied by many workers from the standpoint of process development of terephthalic acid. Only a few references (*1–11*) give information on vapor-phase oxidation of *p*-xylene and meagre data on kinetics are available in the literature (*7, 8, 11*).

Bhattacharyya *et al.* (*1–5*), studying the catalytic vapor-phase oxidation of *p*-xylene and other hydrocarbons, report *p*-tolualdehyde, *p*-toluic acid and maleic anhydride as main products and traces of terephthalic acid and *p*-benzoquinone in fixed bed operation, and two additional products, namely terephthaldehydic acid and terephthaldehyde, using a fluidized bed. However, kinetic analysis was not attempted.

Parks and Allard (*6*) studied the oxidation of mixed xylenes over a number of oxide catalysts and reported their results on the basis of total acids formed. Popova and Kabakova (*7*) studied the kinetics for all the xylenes on a copper catalyst containing heavy metal oxides. The products obtained were aldehydes and CO_2. A general kinetic scheme on gas-phase oxidation of xylenes was reported by Wright (*8*). Barnard and Hawtin (*9*) studied gaseous oxidation of *p*-xylene and showed that the reaction was autocatalytic and that formaldehyde is the degenerated branching intermediate.

Sasayama (*10*) studied the individual oxidation of products like *p*-toluic acid, terephthalic acid over V_2O_5–MoO_3, in the temperature range of 300–430°C to elucidate the mechanism of the oxidation of aromatic hydrocarbons.

Recently Trimm and Irshad (*11*) have studied the influence of electron directing effects on the catalytic oxidation of toluenes and xylenes on molybdenum trioxide. Kinetic work on xylene showed the formation of the hydrocarbon–molybdenum complex to be a slow step.

The present work deals with the kinetics of the oxidation of *p*-xylene over a wide range of temperature and the elucidation of the mechanism of the reaction.

APPARATUS AND PROCEDURE

The experimental assembly consisted of a stainless steel reactor (1.9 cm i.d., 30 cm in length) and separate stainless steel preheaters (2.2 cm i.d.) to heat the reactants. A mixture of air and *p*-xylene after being dried and metered were admitted at different points in the preheater. The partial pressure of oxygen in air was varied by using dried nitrogen. Downward flow of reactants was used in the reactor. A differential reactor was used to facilitate the analysis of the results.

The catalyst was supported on a perforated stainless steel plate (1 mm diam holes) attached to the bottom of the reactor. The amount of the catalyst was varied from 3 to 10 g depending on the variables and exothermicity of the reaction.

p-Xylene was pressurized in a stainless steel still and sent through a calibrated inverted orifice-manometer arrangement and mixed with air drawn at constant pressure from a compressor line also dried in a series of drying traps and metered through a calibrated rotameter. The *p*-xylene flow rates used were in the range 0.022–0.1 g moles/hr and air flow rates varied in the range of 200–350 liters/hr.

The reactor was heated in two portions, the upper portion and the lower catalyst portion in order to control the temperature within ±2°C. The temperatures were measured by a calibrated iron–constantan thermocouple.

Experiments were carried out over a temperature range of 320–420°C, and air: xylene ratio of 480–655. A few experiments were conducted to check the inertness of the reactor. No product was formed in the absence of the catalyst. On the other hand, products were formed when vapors of *p*-xylene reactant were sent over the catalyst in the absence of oxygen or air.

The reaction products were collected in an air condenser, ice-cooled traps and water bubblers. The products before being vented were passed through an ethanol trap to ensure that there was no loss of products. A portion of gas analyzed showed that there were no combustion products formed in the range of temperature studied.

Analytical procedure. The products formed in the reaction were *p*-tolualdehyde, *p*-toluic acid, maleic anhydride and traces of terephthalic acid. The acids were identified by thin layer chromatography (*12*). The tlc analysis was confirmed using authentic samples obtained from BDH (England).

The products were quantitatively analyzed based on the solubility techniques reported by Bhattacharyya and Gulati (*1*) with slight modifications. In the modified method, the reaction products were washed with a minimum quantity of hot distilled water, cooled to 4°C and filtered to remove *p*-toluic and terephthalic acids (if any) which have low solubilities in water at this temperature. The filtrate was added to the aqueous solution from the water traps and analyzed for maleic anhydride and aldehyde. The alcoholic solution from the last trap was also analyzed for the products.

The residue containing *p*-toluic acid and terephthalic acid was washed with chloroform to dissolve *p*-toluic acid. The chloroform extract containing *p*-toluic acid was titrated with alcoholic potash while the residue was dissolved in a known amount of standard alkali and the excess alkali was back-titrated with potassium hydrogen phthalate.

p-Tolualdehyde was identified by its boiling point and also by the melting point of the 2,4-dinitrophenylhydrazine derivative. *p*-Tolualdehyde was analyzed by mixing a known amount of both the alcoholic and aqueous solution so as to obtain better results than by the individual analysis of the two solutions. The aldehyde was estimated by Vogel's (*13*) method which was checked for accuracy using synthetic samples of pure compounds and the error in the estimation was less than 2%.

Materials. The materials consisted of *p*-xylene (Merck grade) of 99.5% purity, nitrogen of over 99% purity and air. Nitrogen and air were dried before use.

The catalyst was prepared by the method given in the literature (*14*). The surface area determined by the BET method was 25.5 m^2/g.

External and internal diffusion. The effect of gas film resistance has been largely overcome by using high velocities of the reactant gas mixture. It was also verified by the method of Yoshida, Ramaswami and Hougen (*15*) which quantitatively evaluates the effect of external mass transfer on reaction rate. The method showed the effect of interphase diffusion to be negligible even at 420°C.

The effect of internal diffusion was studied by using different particle sizes in the range of 0.4–1.4 mm diam. The results showed that the rate of oxidation remained constant for particle size below 0.9 mm, thus indicating the absence of intraparticle diffusion below this size. In the present study, a catalyst size of 0.7 mm was used in the kinetic experiments.

KINETIC ANALYSIS

The variables studied to collect kinetic data under conditions of constant catalytic activity are:

1. Temp, 320–420°C.
2. Concentration of *p*-xylene (C_X), (6.28×10^{-5}–39.7×10^{-5}) moles/liter.
3. Concentration of oxygen (C_O), (2.04×10^{-3}–8.59×10^{-3}) moles/liter.
4. Time factor (W/F), (150–455) g hr/g mole.

The above ranges of variables have been chosen on the basis of preliminary experimentation. In most of the runs, the conversion of *p*-xylene was below 15%. Even at the higher temperature of 420°C at which the conversion was 24%, the error involved in assuming differential reactor operation was 1% as evaluated from the method developed by Massaldi and Maymó (*16*). Even the calculated rates using the redox model have not deviated by more than 10% from the actual rates. The initial rates were also calculated using an approximate equation,

$$\text{initial rate} = (\text{mean rate}) \times \frac{(\text{initial conc of reactant})}{(\text{mean conc of reactant})},$$

as θ (relative concentration of surface oxygen taking part in both the stages of redox model) is fairly constant in the experimental conditions covered. The use of the above equation in calculating the initial rate is justified. The initial rates thus calculated are compared with the experimental rates and the overall deviation is found to be less than 6%. The above analysis shows that the assumption of using a differential reactor is valid. In the present work, the rate is expressed as,

$$r_X = F_X \cdot dx/dW$$

$$\text{where } r_X = \frac{\text{moles of xylene converted}}{\text{sec} \times \text{g of catalyst}}.$$

THEORY

Recent trends in the interpretation of vapor-phase catalytic oxidation reactions on oxide catalysts show the applicability of the two-stage redox model first proposed by Mars and Van Krevelen (*17*). Many oxidation reactions (*17–27*) have been interpreted on the basis of the above model. The steady state redox model of Mars and Van Krevelen (*17*) can be written as:

$$\text{hydrocarbon} + \text{C-ox} \xrightarrow{k\hat{x}} \text{oxidation products} + \text{C-red.}$$

$$\text{C-red} + O_2 \xrightarrow{k\hat{o}} \text{C-ox.}$$

Based on the above model, the rate of oxidation of hydrocarbon (*p*-xylene) is given by,

$$r_X = \frac{k_X k_O C_X C_O}{k_O C_O + N k_X C_X}. \tag{1}$$

Downie *et al.* (*18–23*) have also developed a similar model based on the Hinshelwood concept (*24*) of steady state concentration of reactants on the catalyst surface rather than the equilibrium concentration. The mathematical expressions are identical. They have successfully tested the above model for the oxidation of a number of hydrocarbons, while Mars and Van Krevelen tried the redox model for the oxidation of naphthalene, anthracene and SO_2. Recently the above models have been extended to pseudocumene (*25*) and methanol (*26, 27*) oxidations.

RESULTS AND DISCUSSION

Runs were taken at different concentrations of *p*-xylene keeping the oxygen concentration constant and vice versa. Plots of the linearized form of Eq. (1),

$$\frac{1}{r_X} = \frac{1}{k_X C_X} + \frac{N}{k_O C_O}, \tag{2}$$

as $1/r_X$ vs $1/C_{\hat{X}}$ and $1/r_O$ vs $1/C_O$ resulted in straight lines as shown in Figs. 1 and 2, confirming the validity of Eq. (2) as well as first-order dependence with respect to the concentration of both the reactants.

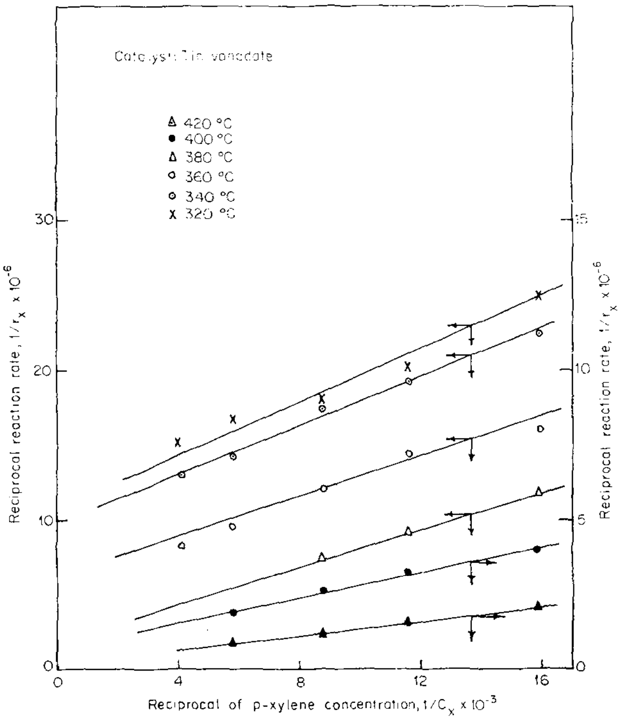

FIG. 1. Plot of $1/C_X$ vs $1/r_X$ at various temperatures.

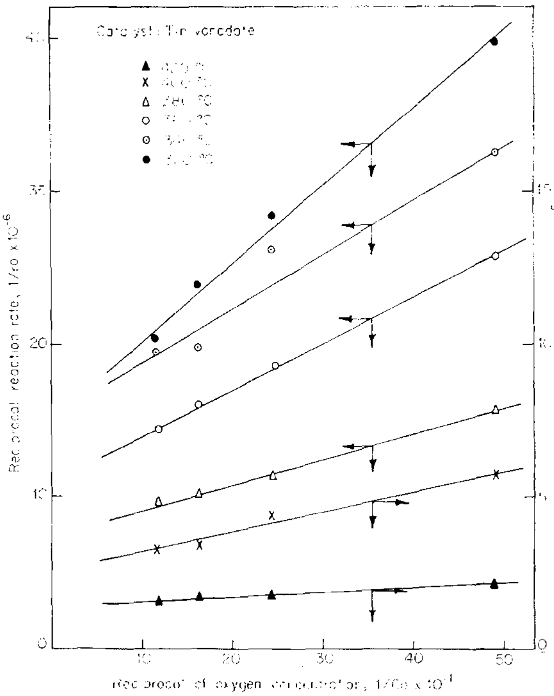

Fig. 2. Plot of $1/C_O$ vs $1/r_O$ at various temperatures.

The data were also tested for 0.5 order with respect to both the reactants, but the rate constants were found to be negative.

The value of N has been evaluated on the basis of the parallel-consecutive scheme (as discussed below).

The values of the rate constants k_X and k_O have been evaluated using the least-squares. k_X and k_O values evaluated by multiple linear regression and nonlinear regression analysis (*28*) are shown in Table 1. The k_X and k_O values evaluated by nonlinear estimation method represent the true values in the equation of the redox model and as the standard deviations are low the nonlinear values of k_X and k_O were used for the evaluation of activation energies and preexponential factors.

The parameters in the Arrhenius equation were also estimated by nonlinear method after reparameterizing the temperature as suggested by Peterson (*29*). Table 2 shows the values of E_X and E_O thus calculated.

Figure 3 shows a change in the activation energy around 370–375°C. Such a break in

TABLE 1

Rate Constants Evaluated Using Multiple Linear Regression and Nonlinear Regression

Temp (°C)	By multiple linear regression			By nonlinear regression		
	$k_X \times 10^3$	$k_O \times 10^5$	SD	$k_X \times 10^3$	$k_O \times 10^5$	SD
420	8.272	104.10	2.27×10^{-8}	8.560	90.17	2.08×10^{-8}
400	4.730	36.94	2.30×10^{-8}	4.630	32.73	1.17×10^{-8}
380	1.610	9.65	0.75×10^{-8}	1.572	9.99	1.14×10^{-9}
360	1.145	5.35	6.27×10^{-8}	1.241	4.28	3.18×10^{-9}
340	0.805	4.10	6.15×10^{-8}	0.953	2.69	4.36×10^{-9}
320	0.786	3.16	2.74×10^{-8}	0.813	2.84	1.95×10^{-9}

TABLE 2

VALUES OF E AND A FOR BOTH THE STEPS BY LINEAR AND NONLINEAR METHOD[a]

Arrhenius activation energy and frequency factor	Temp range (°C)	p-Xylene oxidation step: Linearized estimate	p-Xylene oxidation step: Nonlinear estimate	p-Xylene oxidation step: Av absolute deviation (%)	Oxygen adsorption step: Linearized estimate	Oxygen adsorption step: Nonlinear estimate	Oxygen adsorption step: Av absolute deviation (%)
E	420–380	49.1	48.0	4.1	37.1	32.9	11.3
A	420–380	2.61×10^{12}	3.1×10^{-4}		4.27×10^{9}	4.2×10^{-3}	
E	360–320	8.2	8.9	12.1	6.1	12.7	12.9
A	360–320	2.65×10^{-2}	3.2×10^{-5}		1.58×10^{-1}	3.37×10^{-5}	

[a] The units of E and A are E = kcal g mole^{-1} and A = liter g^{-1} catalyst sec^{-1}.

the Arrhenius plot has been observed previously (*30–33*). This may be due to a possible change in the catalyst structure.

PROBABLE REACTION SCHEME

The oxidation products of p-xylene were p-tolualdehyde, maleic anhydride, p-toluic acid and sometimes traces of terephthalic acid, but no CO_2. As the quantity of terephthalic acid formed was negligible, it was not taken into the reaction scheme.

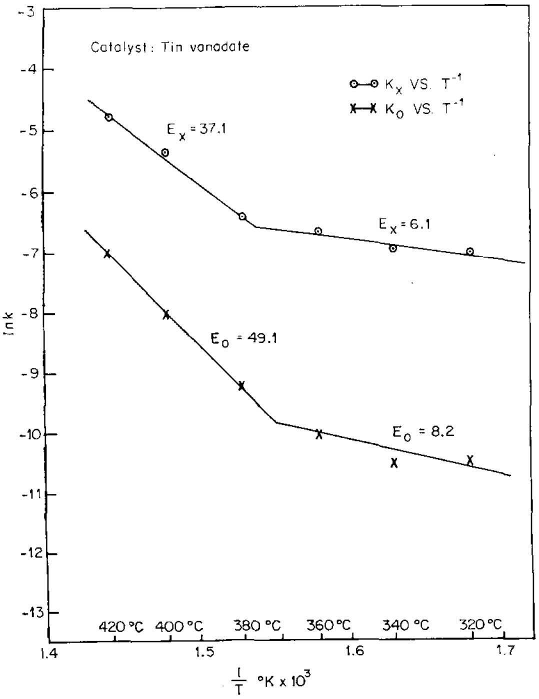

FIG. 3. Arrhenius plot of ln k vs $1/T$.

The series scheme suggested for liquid-phase oxidation of p-xylene does not consider maleic anhydride. In order to find out a particular route for maleic anhydride, individual oxidation of p-tolualdehyde, p-toluic acid and terephthalic acid on tin vanadate was carried out.

The oxidation of p-tolualdehyde gave 2.7 and 5% of p-toluic acid and 2.5 and 7.5% of CO_2 at two W/F ratios, i.e., 50 and 200, respectively, keeping the air:aldehyde ratio at 40. The product distribution was identical in both cases. This confirms that p-toluic acid is formed from p-tolualdehyde as reported in liquid phase and this product is not formed from p-xylene directly. The oxidation of p-toluic acid and terephthalic acid gave only CO_2. Maleic anhydride was not formed from any of the individual oxidation products. As maleic anhydride is present in the products of oxidation only, a parallel-consecutive mechanism seems likely.

The reaction scheme considered may be stoichiometrically written as

$$C_8H_{10} + O_2 \xrightarrow{k_1} C_8H_8O + H_2O$$

$$C_8H_{10} + 4.5\ O_2 \xrightarrow{k_2} 2\ C_4H_2O_3 + 3\ H_2O$$

$$C_8H_8O + 0.5\ O_2 \xrightarrow{k_3} C_8H_8O_2.$$

In the above scheme p-tolualdehyde and maleic anhydride are formed from p-xylene. A part of p-tolualdehyde is converted to p-toluic acid. In all the runs the ranges of maximum and minimum conversions of the different products are:

p-tolualdehyde	21–2.0%
maleic anhydride	8–1.0%
p-toluic acid	3–0.1%

Because of the high flow rates of air used, the rate equations for the above reactions, assuming pseudo-first-order kinetics are:

For *p*-xylene disappearance:

$$-\frac{dC_X}{d(W/F)} = (k_1 + k_2)C_X. \qquad (3)$$

For *p*-tolualdehyde formation:

$$\frac{dC_T}{d(W/F)} = k_1C_X - k_3C_T. \qquad (4)$$

For maleic anhydride formation:

$$\frac{dC_M}{d(W/F)} = 2k_2C_X. \qquad (5)$$

For *p*-toluic acid formation:

$$\frac{dC_{T'}}{d(W/F)} = k_3C_T, \qquad (6)$$

where C_X = p-xylene; C_T = *p*-tolualdehyde; C_M = maleic anhydride; $C_{T'}$ = *p*-toluic acid.

Equations (3) and (4) on integration give,

$$C_X = C_{Xo}e^{-(k_1+k_2)(W/F)} \qquad (7)$$

and

$$C_T = \frac{k_1C_{Xo}}{k_3 - (k_1 + k_2)} \times [e^{-(k_1+k_2)(W/F)} - e^{-k_3(W/F)}]. \qquad (8)$$

Equation (8) can be modified as

$$X_T = \frac{k_1}{(k_1 + k_2 - k_3)} \times [e^{-k_3(W/F)} - e^{-(k_1+k_3)(W/F)}], \qquad (9)$$

where $C_T = C_{Xo}X_T$.

Equations (5) and (6) can be integrated to give C_M and $C_{T'}$.

Equation (7) on rearrangement gives,

$$\ln C_{Xo}/C_X = (k_1 + k_2)(W/F), \qquad (10)$$

or

$$\ln\left(\frac{1}{1 - X_t}\right) = (k_1 + k_2)(W/F). \qquad (11)$$

The value of $(k_1 + k_2)$ was evaluated by least-squares technique.

Parallel mechanism. The individual values of k_1 and k_2 were evaluated from the relations

$$\ln\left(\frac{1}{1 - X_T}\right) = k_1(W/F), \qquad (12)$$

and

$$\ln\left(\frac{1}{1 - X_M}\right) = k_2(W/F), \qquad (13)$$

and the sum of the values was found to be nearly equal to the total value obtained from Eq. (11) justifying the assumption of the parallel mechanism.

The parallel mechanism was rechecked by adding *p*-toluic acid equivalent to *p*-tolualdehyde (as *p*-toluic acid was formed from *p*-tolualdehyde). The sum of the values of k_1 obtained by this method and k_2 obtained by Eq. (13) found by least-squares method was almost equal to $(k_1 + k_2)$ obtained from Eq. (11), thus confirming the validity of the parallel scheme.

Parallel-consecutive mechanism. Once it is ascertained that the parallel scheme is applicable, the parallel-consecutive scheme was tested by evaluating k_1, k_2 and k_3. k_2 was evaluated by using Eq. (13) and the value of k_1 from the relation

$$\left(\frac{X_T}{1 - X_t}\right) = k_1(W/F). \qquad (14)$$

Equation (14) can be obtained from Eqs. (8) and (7) and using the relations $C_T = C_{Xo}X_T$ and $C_X = C_{Xo}(1 - X_t)$.

The value of k_1 thus obtained was 1.98 × 10^{-4} and the value obtained by evaluating the sum of values of $(k_1 + k_2)$ was 2.18 × 10^{-4}; k_3 was evaluated by a trial and error procedure using Eq. (9).

The different values of k_1, k_2, k_3 and k obtained at 360°C are

$k_1 = 1.98 \times 10^{-4}$, $k_3 = 0.82 \times 10^{-4}$,
$k_2 = 0.535 \times 10^{-4}$, $k = 2.72 \times 10^{-4}$.

Test of the calculated values of k_1, k_2, k_3. The values of W/F versus conversion for different air:xylene ratios, the total disappearance [Eq. (7)] and the expected

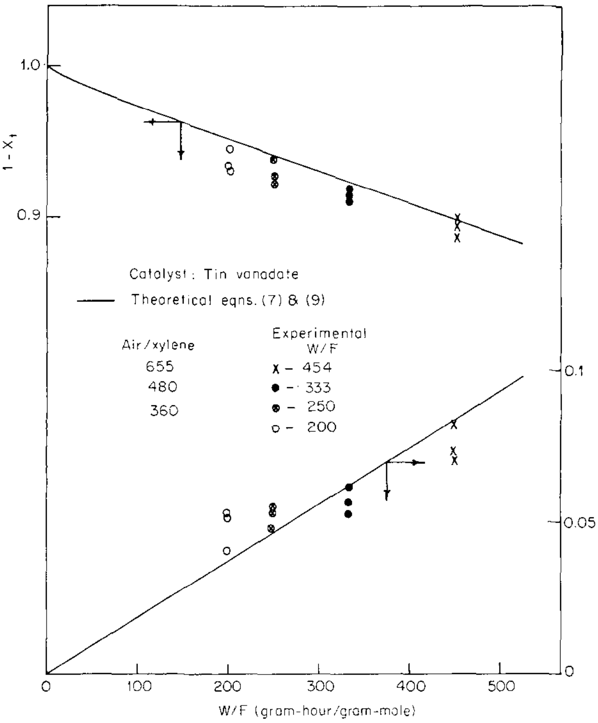

FIG. 4. Comparison of Eqs. (7) and (9) with experimental data for *p*-tolualdehyde formation and total *p*-xylene conversion.

conversion to *p*-tolualdehyde [Eq. (9)] have been calculated using the values of k_1, k_2, k_3 and $(k_1 + k_2)$ (as mentioned above) and compared with the experimental results, as shown in Fig. 4. The agreement is good with an average deviation of 0.9 and 11.8% for the disappearance of xylene and formation of tolualdehyde, respectively.

CONCLUSION

Kinetic analysis indicates the validity of redox model. A break in the Arrhenius plot was observed around a temperature of 370°C with a sixfold increase in activation energy. This behavior may be due to an unfavorable orientation of the lattice, i.e., a change in the catalyst structure.

The reaction was found to follow a parallel-consecutive route.

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