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Analysis of the Reaction Network for the Vanadia-Catalyzed Oxidation of Ortho-Xylene

I. F. BOAG,[1] D. W. BACON AND J. DOWNIE

Department of Chemical Engineering, Queen's University,
Kingston, Ontario, Canada

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The oxidation of *o*-xylene over a vanadium oxide catalyst was studied using a recirculation reactor over the following ranges of conditions: 310 to 330°C oxygen feed concentration (0.25 to 0.75) × 10^{-2} g moles/liter, *o*-xylene feed concentration (0.5 to 3.0) × 10^{-4} g moles/liter, conversion 8 to 75%.

The combination of a recirculation reactor and a quantitative rate modeling approach was shown to provide an effective method for the characterization of reaction networks which should be useful for catalyst screening and optimization studies. The extended form of the steady-state adsorption model was shown to provide a satisfactory description of the vanadia-catalyzed oxidation of *o*-xylene at high conversions with significant secondary reactions.

NOMENCLATURE

C_h	concentration of compound h_i, an immediate predecessor of i, g moles/liter
C_i	concentration of compound i, g moles/liter
C_o	concentration of oxygen, g moles/liter
k_a	rate constant for oxygen adsorption, liters/g catalyst sec
k_{hi}	rate constant for the reaction of h to i, liters/g catalyst sec
k_{ij}	rate constant for the reaction of i to j, liters/g catalyst sec
n_{ij}	moles of oxygen required (per mole of compound i) for the reaction of i to j
r_i	rate of reaction of compound i, g moles/g catalyst sec
s_{pe}^2	estimate of pure error variance
s_{lf}^2	mean square due to lack of fit plus pure error
$\sum nkc$	$\sum_i \sum_j n_{ij}k_{ij}C_i$, where i and j represent reactants in all reaction steps, where $j > i$.

INTRODUCTION

The analysis of multistep reaction networks has traditionally been done by subjective interpretation of product distribution data. The method is sound but somewhat limited in scope and provides mainly qualitative information. The aim of the present work was to develop and test an efficient experimental approach for the quantitative analysis of a complex reaction network. The method involves the application of rate modeling techniques to data gathered in a recirculation reactor and the use of statistical techniques for experimental design and data analysis.

The reaction studied was the vanadia-catalyzed oxidation of *o*-xylene. This reaction has been studied by a number of workers (*1–5*), most of whom have presented reaction networks based on qualita-

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[1] Present address: Department of Industrial Management & Engineering, Massey University, Palmerston North, New Zealand.

tive analysis of changes in selectivity with conversion or space time. In addition, some of these studies have "over-interpreted" the data, i.e., have drawn more conclusions than could be supported by the data. For example, Herten and Froment (4) decided that all products were formed in primary reaction steps, but this conclusion was based on the initial slopes of selectivity curves extrapolated back to zero conversion from their lowest value of 25%. They also postulated the existence of several secondary reactions for which their data did not provide any direct support. Another example is found in the work of Simard *et al.* (1), who proposed that phthalic anhydride was a stable product on the basis of data for which the conversions did not exceed 25%.

It should be noted that the reaction schemes reported by different workers showed marked differences, which can probably be ascribed to the use of different catalysts. The results of Kakinoki *et al.* (6,7) and Wainwright (8) indicated that the activity and selectivity for *o*-xylene oxidation are strongly affected by the catalyst support chosen and by the level of sulfur-bearing compounds in the catalyst. In both cases, silica-supported catalysts were found to give a lower yield of phthalic anhydride than other types.

Some workers (9,10) have also oxidized intermediate products in order to define the secondary reactions. However, the nature of the catalyst/reactant interaction is such that results obtained from such work do not necessarily represent the processes occurring on the catalyst when the primary reactant is also competing for catalytic sites. This is borne out by the results of Lyubarskii *et al.* (9), who found that the reactions of some of the products were strongly inhibited by the presence of other reacting species.

In the present study a quantitative approach was used in which the overall network was represented by a kinetic model and inferences about the existence and significance of each reaction step were drawn from the magnitude and precision of the corresponding rate constant. In order to ensure that the experiments performed were of the greatest possible utility for this purpose the homoscedastic version of the multiresponse sequential experimental design strategy of Box and Draper (11) was used in planning the experimental program. This method involves the selection, at each stage, of the experimental run which gives the greatest decrease in the determinant of the parameter covariance matrix and leads to a sequence of runs which gives the most precise estimates of the model parameters. The method also indicates the rate at which the limits of resolution of the experimental system are being approached, i.e., evidence of the improvement in the precision of the parameters to be expected from further experimental runs.

The kinetic model used for describing the network in this study was a multiresponse form of the steady-state adsorption model which was first presented in this extended form by Juusola *et al.* (12). This model was selected because it was the best of several that Juusola had tested on low-conversion *o*-xylene oxidation data, and because it offered a more economical parameterization of the system for modeling the network than any of the other models considered. The form of the model rate expressions is:

$$r_i = \left(\sum_j k_{ij} C_i - \sum_h k_{hi} C_h\right) \theta,$$

where θ, the fractional coverage of the surface by adsorbed oxygen, is given by:

$$\theta = k_a C_o / (k_a C_o + \Sigma nkC).$$

The model was fitted by minimization of the determinant of sums of squares and cross-products of residuals, a procedure developed by Box and Draper (13).

The advantages of a recirculation reactor over the tubular type have been summarized by Carberry (*14*). In brief, it offers better control over particle–fluid gradients and easier maintenance of isothermal conditions, but at some cost in flexibility and in selectivity for intermediate products. Also, the component mass balances for such a reactor are algebraic, rather than differential equations and one might suspect this would simplify quantitative data analysis. Several types of recirculation reactors have been described in the literature (*14–16*) and a comparison of their relative strengths and weaknesses led to the adoption for this work of a design similar to that used by Weychert and Trela (*16*).

EXPERIMENTAL METHODS

Oxygen and nitrogen flows were measured on resistance flowmeters and controlled by needle valves, and *o*-xylene and SO_2 were fed from syringes driven by syringe pumps. No feed preheat was necessary as the residence time in the reactor was of the order of 40 sec and the reactor contents were well mixed.

An exploded view of the 304 stainless steel recirculation reactor used for this work is presented in Fig. 1. The reactants flowed down the outer wall and back up through the catalyst bed in the central tube. The feed stream entered through the reactor lid, except for a small flow of nitrogen (about 5% of the total) which was introduced around the shaft to prevent any organic material from condensing on the cool face of the shaft seal. The reactor was heated by a snug-fitting aluminum block containing four cartridge heaters. The temperature was measured and controlled from an iron–constantan thermocouple in-

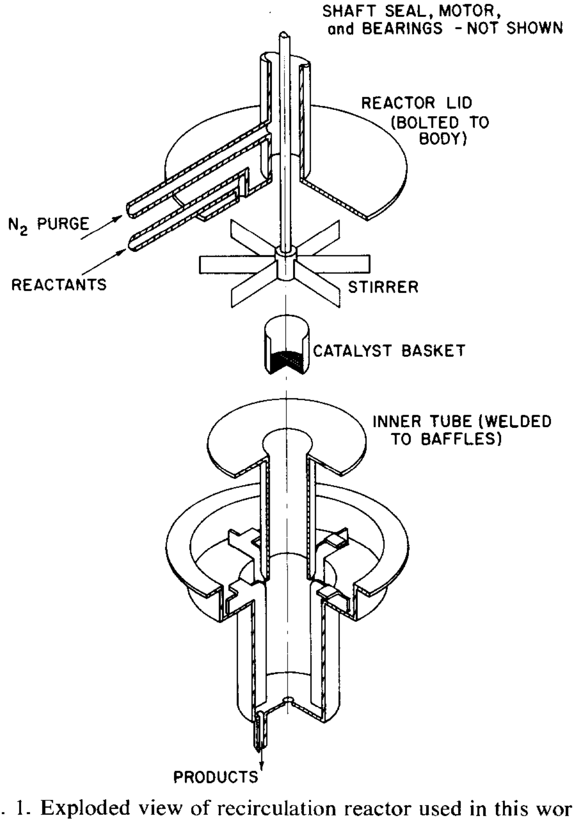

FIG. 1. Exploded view of recirculation reactor used in this work.

serted through the bottom of the reactor to a point just below (i.e., before) the catalyst bed.

The impeller rotational speed was 4500 rpm. A series of step response tests was conducted with the catalyst replaced by glass beads and these showed that the perfect mixing assumption was valid for this reactor. Therefore, the CSTR mass balance equations could be used for quantitative data analysis.

Organic products and unreacted *o*-xylene from each run were collected in glass traps cooled by dry ice. At the end of the run the trap was warmed to room temperature and the contents were washed out with acetone for quantitative analysis by gas chromatography. During the run samples of the effluent gases were analyzed for carbon oxides, also by gas chromatography.

The catalyst was vanadium oxide, potassium sulfate promoted, on a silica carrier. The surface area was 70 m^2/g. Further details are available in Ref. (*17*) and (*18*). The catalyst was supplied by Grace-Davison Chemical Co.

Procedure

After the reactor temperature had stabilized, the feed conditions were set and the system was left running for 60 to 90 min to allow the catalyst to reach steady-state conditions. The trap was then connected and the run commenced; runs lasted from 30 to 120 min depending on the amounts of products needed for analysis.

The effluent gases were analyzed at intervals throughout the run for carbon monoxide (on a 6 ft column containing 60/80 mesh molecular sieve 13X) and carbon dioxide (on a 12 ft column containing 30% diethyl hexyl sebacate on 60/80 mesh Chromosorb P). Both analyses were performed at room temperature. At the end of the run the washings from the trap were diluted to a standard volume and analyzed by injecting a sample into a 10 ft column containing 10% SE-52 silicone gum rubber on 60/80 mesh acid washed Chromosorb W. This column was programmed from 75 to 180°C at 10°C/min to separate all the organic products. Carbon balances on the feed and the products agreed satisfactorily.

The ranges of feed concentrations and temperatures were as follows: xylene feed concentration $(0.5 \text{ to } 3.0) \times 10^{-4}$ g moles/liter, oxygen feed concentration $(0.25 \text{ to } 0.75) \times 10^{-2}$ g moles/liter, temperature 310 to 330°C. A total feed rate of 0.5 liters/min at reactor conditions and a catalyst charge of 4.5 g of 8/10 mesh particles were used for all runs. The SO_2 level in the feed was maintained at 0.1% by volume.

DISCUSSION OF RESULTS

The main organic products found in the present study were: *o*-tolualdehyde, *o*-phthalaldehyde, phthalide, and phthalic anhydride. In addition there were a number of minor products (maleic anhydride, toluene, *p*-benzoquinone and others) but since these only aggregated to about 4% of the reaction they were not considered individually. Carbon dioxide and carbon monoxide occurred in the same relative proportions (3:1) for all feed conditions and were lumped together and considered as a single product to simplify analysis of the data.

Before a heterogeneous-type rate model could be applied to the data it was necessary to evaluate the extent of the blank reaction. Tests were conducted with no catalyst in the reactor and these showed that *o*-tolualdehyde was relatively unstable. The results of these runs were fitted by homogeneous-type rate expressions in order to derive a blank correction for catalytic data. The application of such a correction to CSTR data is a simple matter because all concentrations are uniform throughout the reactor. The correction varied from 5 to 20% of the net rate of *o*-tolualdehyde formation. The blank reaction of *o*-tolualdehyde yields the same products as the overall reaction.

Checks for mass-transfer control of the reaction were conducted using standard methods. These showed that neither external nor pore diffusion was rate controlling. The criteria for heat transport limitations in fixed bed reactors proposed by Mears (*19*) were used to check that the temperature rise of the catalyst particles was insignificant. The criteria were satisfied. Details are given in Ref. (*18*).

The catalyst activity underwent a slow decline over the period of 250 hr that the catalyst was on stream. For the initial series of runs in elucidating the reaction network this decline was relatively small (of order 6–8%) and it was ignored. The effect of this action was to give an inflated estimate of the experimental error variance and therefore decrease the precision of the estimated rate constants; since the precision of the final parameter estimates was acceptable this procedure was considered reasonable. However, for later work involving the temperature dependence of the rate constants, it was necessary to correct several sets of rate constants, from different ages and temperatures, to a common activity basis in order to draw an Arrhenius plot. This was done by factoring each rate constant with an appropriate aging function estimated from the results of fitting the model to data gathered at widely different catalyst ages. The estimated value of k_a was found to be essentially unchanged as the catalyst activity declined.

Figure 2 shows the results from a preliminary set of 15 scouting runs at 320°C presented as a plot of yield (corrected for blank reaction) against conversion. These are typical of the results obtained in this work, and it is evident that both primary and secondary reactions are significant. The solid lines were drawn in by eye to facilitate interpretation of the data. Table 1 lists the products and all 14 possible reaction steps in the network.

The results in Fig. 2 suggest that *o*-

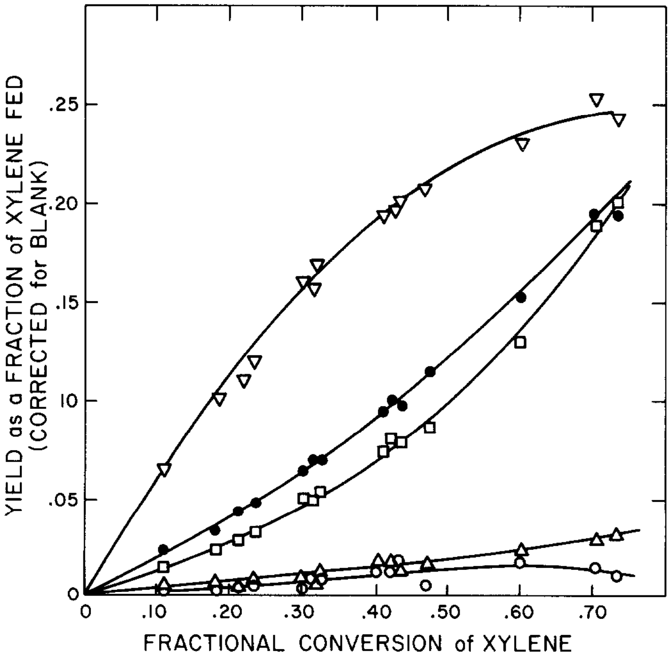

FIG. 2. Typical yield versus conversion data at 320°C. (▽) *o*-tolualdehyde; (○) *o*-phthaldehyde; (△) phthalide; (□) phthalic anhydride; (●) carbon oxides.

TABLE 1
POSSIBLE OXIDATION STEPS

	Substance	Formula	Possible reactions				
1	*o*-Xylene	C_8H_{10}	1→2	1→3	1→4	1→5	1→6
2	*o*-Tolualdehyde	C_8H_8O	2→3	2→4	2→5	2→6	
3	*o*-Phthalaldehyde	$C_8H_6O_2$	3→5	3→6			
4	Phthalide	$C_8H_6O_2$	4→5	4→6			
5	Phthalic anhydride	$C_8H_4O_3$	5→6				
6	Carbon oxides	$CO_2 + CO$					

tolualdehyde is an unstable primary product and that phthalic anhydride and carbon oxides are stable products formed in both primary and secondary reaction steps. The roles of phthalide and *o*-phthalaldehyde are more difficult to assess because these are relatively less significant products and there is more scatter in the results.

It should be noted that there are two factors which tend to confuse the interpretation of the data in Fig. 2. The first is that conclusive identification of a stable product is not possible from examination of product distribution data gathered at conversions of less than 100%. For example, in the case of phthalic anhydride the yield curve does not tell us whether the 56 reaction is negligible or whether it is significant but masked by another step such as a 45 reaction step. The second point is that each of the data points shown corresponds to a different set of feed concentrations. In view of the fact that mutual inhibition effects are known to be important for this system as demonstrated by Lyubarskii and Petoyan (*15*) it is possible that the product distribution may not be a unique function of conversion and this fact weakens the qualitative analysis of such yield data.

Because of these uncertainties a conservative approach was used for modeling the reaction in that the network model fitted to the data included all the 14 possible steps listed in Table 1.

After the model had been fitted to the initial 15 run data set, further runs were executed following the precise parameter estimation design strategy of Box and Draper (*11*). A total of 36 runs were performed and examination of trends in the precision of the parameter estimates with increases in the size of the data set revealed that the parameter estimates from these runs were for all practical purposes the most precise available from this experimental system. Further runs would not have given any significant improvement.

Analysis of the results from fitting the full network model to this 36 run data set then enabled several simplifications to be made. It was found that the model did not satisfactorily describe the net rate of *o*-phthalaldehyde formation, and in addition the parameters related to its formation and reaction were very poorly estimated (i.e., had large standard errors and were highly correlated with other parameter estimates). It was concluded that some of the minor products neglected in the network formulation were probably formed from *o*-phthalaldehyde. Since *o*-phthalaldehyde was the least important of the major products (of the order of 3% of the reaction) the solution adopted for this difficulty was to delete it from the network model and combine it with the minor products. The average fraction of the products composed of *o*-phthalaldehyde and the minor products was about 6.5%. Further simplifications were also effected by deleting those parameters for which the estimated values were indistinguishable from zero.

The final network obtained after this procedure is shown in Fig. 3; the width of

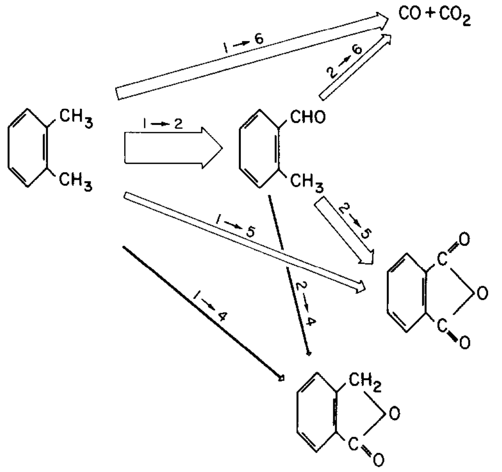

FIG. 3. Final reaction network.

each arrow is proportional to the magnitude of the corresponding estimated rate constant. This gives a pictorial representation of the point estimates of the rate constants without attempting to reflect the precision of these estimates. Table 2 lists the estimated parameter values with their 95% confidence intervals, and also shows the results of approximate lack of fit tests described by Draper and Smith (*20*). Comparison of the values of the ratio (s_{lf}^2/s_{pe}^2) with the appropriate tabulated F value revealed no lack of fit. Figures 4 to 8 show observed values and curves from the fitted multiresponse model for the xylene conversion and product distribution as functions of the feed concentrations of oxygen

TABLE 2

PARAMETER ESTIMATES AND ANALYSIS OF VARIANCE FROM THE SIMPLIFIED MODEL AT 320°C

Parameter estimates

k_a	$0.874 \times 10^{-4} \pm 0.200 \times 10^{-5}$
k_{12}	$0.405 \times 10^{-2} \pm 0.363 \times 10^{-3}$
k_{14}	$0.209 \times 10^{-3} \pm 0.226 \times 10^{-4}$
k_{15}	$0.832 \times 10^{-3} \pm 0.105 \times 10^{-3}$
k_{16}	$0.134 \times 10^{-2} \pm 0.140 \times 10^{-3}$
k_{24}	$0.146 \times 10^{-3} \pm 0.350 \times 10^{-4}$
k_{25}	$0.151 \times 10^{-2} \pm 0.160 \times 10^{-3}$
k_{26}	$0.972 \times 10^{-3} \pm 0.180 \times 10^{-3}$

Approximate Lack of Fit Tests[a]

Response	1	2	4	5	6
s_{lf}^2/s_{pe}^2	1.27	1.66	0.72	1.21	1.39

$F_{(9,25,0.95)} = 2.34$

[a] Degrees of freedom for each response: $\nu_{tot} = 34$, $\nu_{pe} = 25$, $\nu_{lf} = 9$.

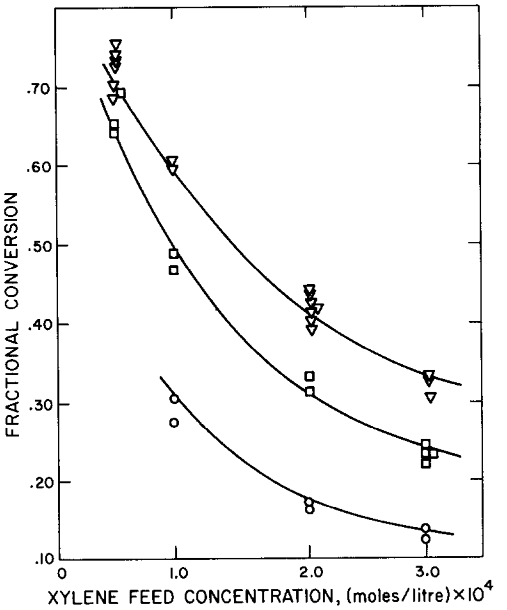

FIG. 4. Xylene conversion as a function of oxygen and xylene feed concentrations at 320°C. Oxygen concn (g moles/liter): (○) 0.25×10^{-2}; (□) 0.50×10^{-2}; (▽) 0.75×10^{-2}.

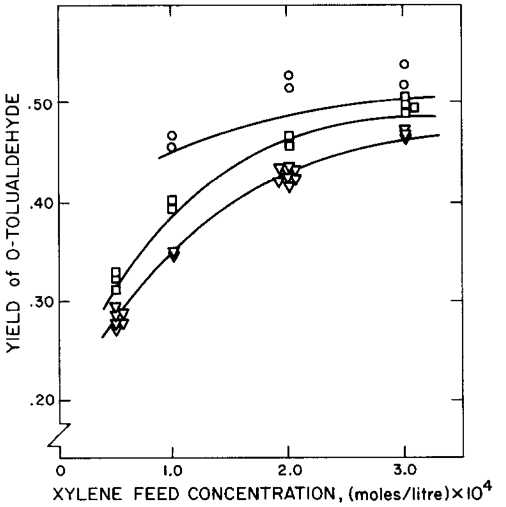

FIG. 5. Yield of *o*-tolualdehyde as a function of oxygen and xylene feed concentrations at 320°C. Oxygen concn (g moles/liter): (○) 0.25×10^{-2}; (□) 0.50×10^{-2}; (▽) 0.75×10^{-2}.

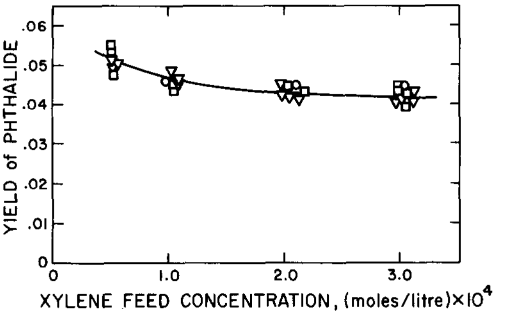

FIG. 6. Yield of phthalide as a function of oxygen and xylene feed concentrations at 320°C. Oxygen concn (g moles/liter): (○) 0.25×10^{-2}; (□) 0.50×10^{-2}; (▽) 0.75×10^{-2}.

and *o*-xylene. The agreement is satisfactory, although there is some bias in the *o*-tolualdehyde and carbon oxide predictions at low oxygen concentrations.

Further work was then carried out to investigate the temperature dependence of the rate constants. The network model was fitted to three data sets gathered at 310, 320, and 330°C and the rate constants obtained were corrected to a standard catalyst age of 150 hr. The model was adequate at each temperature. Figures 9 and 10 show these rate constants (with their 95% confidence intervals) on Arrhenius plots. The confidence intervals for k_a were too small to show on this plot. For all cases except k_{24} (the *o*-tolualdehyde–phthalide step) the rate constants follow the Arrhenius law.

The anomalous behavior of k_{24} can be explained from statistical and physical considerations. At each temperature it is evident that k_{24} is not well estimated and the width of the confidence interval is such that a negative slope on the Arrhenius plot is not implausible. Also, this particular reaction step was masked by blank reac-

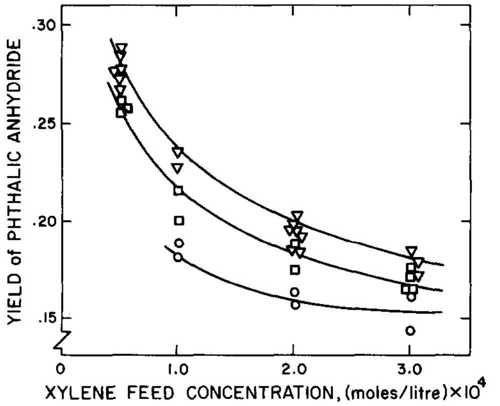

FIG. 7. Yield of phthalic anhydride as a function of oxygen and xylene feed concentrations at 320°C. Oxygen concn (g moles/liter): (○) 0.25×10^{-2}; (□) 0.50×10^{-2}; (▽) 0.75×10^{-2}.

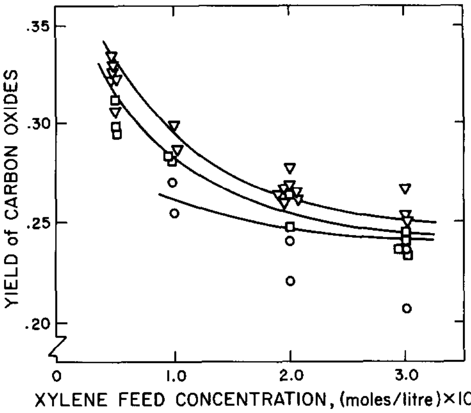

FIG. 8. Yield of carbon oxides as a function of oxygen and xylene feed concentrations at 320°C. Oxygen concn (g moles/liter): (○) 0.25×10^{-2}; (□) 0.50×10^{-2}; (▽) 0.75×10^{-2}.

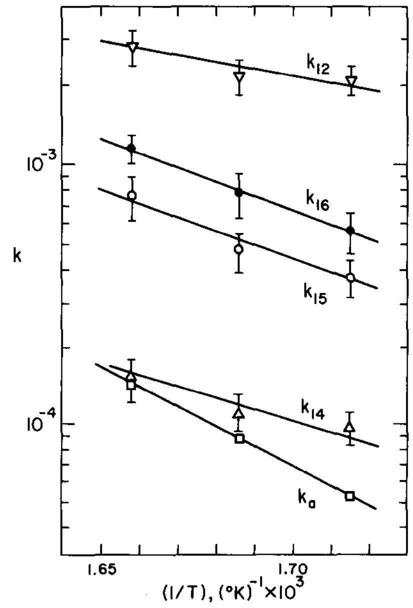

FIG. 9. Arrhenius plot for k_a and the primary rate constants.

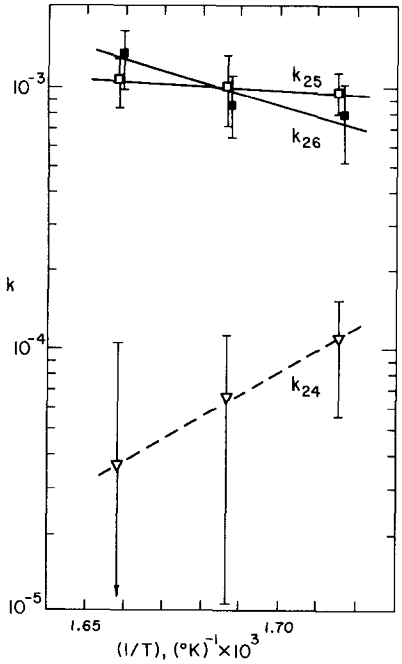

FIG. 10. Arrhenius plot for the secondary rate constants.

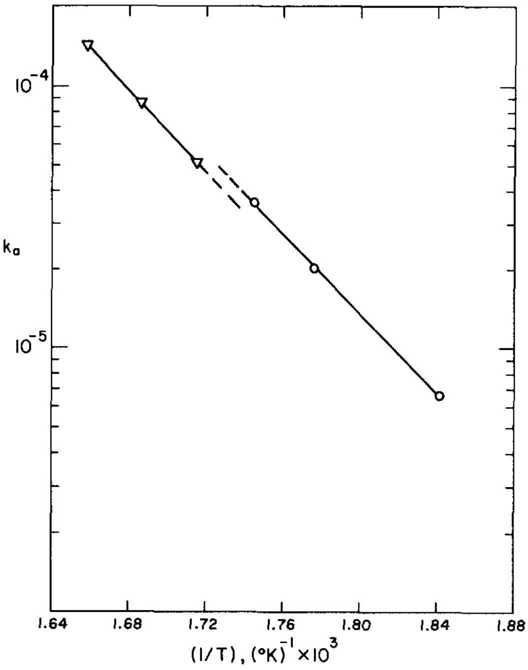

FIG. 11. Comparison between the k_a values from this work (▽) and those reported by Juusola *et al.* (*21*) (○).

tion and this blank could not be measured very accurately. The estimate of k_{24} is of course strongly dependent on the magnitude of the calculated blank correction. Thus it would seem that the apparent negative activation energy for this rate constant is a spurious result, and does not provide grounds for rejection of the model.

Since the value of k_a, the oxygen adsorption rate constant, had been found to be independent of catalyst age, a comparison was made between the k_a estimates from this work and those obtained by Juusola *et al.* (*21*) in their differential-bed study of the reaction at lower temperatures, using the same catalyst. Figure 11 shows the two sets of k_a values on an Arrhenius plot and reveals the agreement to be satisfactory.

Examination of the rate constants in the final network (Table 2) shows that the ultimate yield of phthalic anhydride at 100% xylene conversion is about 45%. This is considerably lower than the 70% obtained in industrial practice, and corroborates the findings of Kakinoki *et al.* (*6, 7*) and Wainwright (*8*) concerning the yield limitations of silica-supported catalysts for this reaction.

CONCLUSIONS

The combination of a recirculation reactor and the quantitative rate modeling approach used in this work has been shown to provide an effective method for the characterization of reaction networks which should be useful for catalyst screening and optimization studies.

The extended form of the steady-state adsorption model is suitable from both statistical and chemical standpoints for describing the vanadia-catalyzed oxidation of *o*-xylene at high conversions with significant secondary reactions.

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