Oxidation of *o*-Xylene to Phthalic Anhydride over V_2O_5/TiO_2 Catalysts

Part 4. Mathematical Modelling Study and Analysis of the Reaction Network

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Results previously obtained for the oxidation of *o*-xylene and *o*-tolualdehyde over a 1% V_2O_5/TiO_2 catalyst have been subjected to mathematical modelling, using comprehensive "rake" networks which incorporate adsorbed intermediates, a variety of routes to CO_2, and provision for the formation and removal from the surface of a "residue" formed at low conversion by both reactants. Equations representing yields of products as a function of reactant conversion are presented; these contain series of parameters that are complex functions of the rate constants for the individual steps, their values being obtained by regression analysis. The modelling confirms that phthalic anhydride is formed through a sequential process involving adsorbed forms of *o*-tolualdehyde and phthalide as intermediates, but it is not formed by direct conversion of *o*-xylene and *o*-tolualdehyde. At high conversion, phthalic anhydride selectivity generally passes through a maximum, showing that it can undergo further oxidation to CO_2. The selectivity for the "residue" (S_R) also passes through a maximum as it is removed from the surface; moreover, the initial slopes of S_R vs conversion curves show that the "residue" is formed early in the reaction network. © 1996 Academic Press, Inc.

INTRODUCTION

The kinetics of the oxidation of *o*-xylene to phthalic anhydride have been studied by several workers, and models of different complexity have been proposed; however, since they involve different catalysts, promoters, and experimental conditions, their comparison and the achievement of valid conclusions has been difficult. These models have been discussed by Wainwright and Foster (1) and, more recently, by Nikolov *et al.* (2), and they show that the modelling has been made primarily on the basis of the Mars and van Krevelen mechanism (3) and the steady state adsorption model (SSAM) (4).

Herten and Froment (5), studying the oxidation of *o*-xylene on a V_2O_5 catalyst, have shown that the rate of conversion of xylene is described equally well by both the power law and the Mars and van Krevelen equation. In 1977, Calderbank *et al.* (6) studied the kinetics of the cata-lysed air-oxidation of *o*-xylene to phthalic anhydride over various commercial V_2O_5/TiO_2 catalysts, finding that, at lower reactant concentrations, the rate of *o*-xylene conversion was proportional to its concentration and that, in the 613–713 K range, rates were almost independent of the oxygen partial pressure, but became increasingly dependent as the temperature was raised. At higher temperatures and higher xylene concentration, the reaction tended towards a zero order with respect to xylene and first order with respect to oxygen. They also used the redox kinetic model in a study of a tubular reactor, considering a reaction network where *o*-xylene and phthalic anhydride were the only sources of CO_2, and phthalic anhydride could result directly from *o*-xylene or from the *o*-xylene → *o*-tolualdehyde → phthalide sequence. A similar reaction network, where the total oxidation of phthalic anhydride was suppressed, was subsequently developed (7), temperature and concentration profiles along the reactor being calculated and compared with experimental data. A more complex parallel-consecutive reaction network has later been proposed (8), but the redox model was not considered adequate for a complete description of the system. The Langmuir–Hinshelwood kinetic model, in which a surface reaction between *o*-xylene and oxygen, chemisorbed on separate active centres, is the limiting step, was preferred; rate equations obtained being in good agreement with the experimental results. The steady-state adsorption model, mathematically equivalent to that proposed by Mars and van Krevelen, has also been reported as giving a good description of the kinetics of *o*-xylene oxidation over silica-supported catalysts (9, 10).

Statistical methods have been used in the study of the reaction network (11–13). Boag *et al.* (12) described the application of a statistical multiresponse method for the V_2O_5-catalysed oxidation of *o*-xylene in a recirculation reactor. A consecutive–parallel reaction network was proposed, its significant steps being identified. A similar mathematical treatment was performed by McLean *et al.* (13) who, in order to improve the precision of the rate constants associated with secondary and tertiary steps of the reaction network,

also used mixed reactor feeds, consisting of mixtures of *o*-xylene, *o*-tolualdehyde, and oxygen.

Pant and Chanda (14) studied the kinetics of the reaction over a V_2O_5 catalyst in the 723–790 K range, using a continuous stirred tank reactor. The pattern of product distribution suggested a parallel reaction scheme in which phthalic anhydride, maleic anhydride, and carbon dioxide were formed from *o*-xylene by parallel routes. The reaction was well represented by assuming it to be first order in both *o*-xylene and oxygen, and applying the redox model. Studies published by Wainwright and Hoffman (15, 16) were also based on the redox model. The analysis of the reaction kinetics by using the redox mechanism and a reaction network where *o*-tolualdehyde, phthalide, and phthalic anhydride were sequentially obtained from *o*-xylene, and the products of total oxidation were obtained only from *o*-xylene and *o*-tolualdehyde, was attempted. However, results have shown that such a model was not adequate to describe all reactions considered.

The mathematical modelling of kinetic results in heterogeneous catalysis has been thoroughly analysed by Froment (17). For the oxidation of *o*-xylene, considering the network proposed by Vanhove and Blanchard (18), where *o*-xylene is the only source of CO and CO_2, he has proposed several rate equations, depending on the partial pressure of the reactant and intermediates. Those can be used in the quantitative treatment of the kinetic results by means of integral or differential methods.

Papageorgiou *et al.* (19) have recently published the results of their kinetic study of this reaction and have concluded that *o*-xylene is the only source of CO_2, although their reaction scheme does not include other possible routes might later have been eliminated by the modelling operation. By working only at high conversion, they failed to observe formation of "residue," although it is possible that this does not occur on their catalyst; however, they give no detailed information on its characterization, so that further speculation as to the causes of the differences between our work and theirs is fruitless.

The oxidation of reaction intermediates has been also performed. Lyubarskii *et al.* (20) have studied the kinetics of the oxidation of *o*-tolualdehyde and phthalic anhydride over V_2O_5 catalysts, in the 713–773 and 663–733 K temperature ranges, respectively. The oxidation of phthalic anhydride yielded only maleic anhydride and products of total oxidation, a consecutive–parallel scheme being proposed, whereas, for *o*-tolualdehyde oxidation, a parallel scheme was considered.

In the present paper, results previously obtained (21) for the oxidation of *o*-xylene and *o*-tolualdehyde are subjected to mathematical modelling, using comprehensive reaction networks. This is part of a detailed study of the *o*-xylene oxidation that includes experiments performed at lower temperatures and shorter contact times (21–23), allowing

the study of the formation of "residue," frequently mentioned (24–27) but never considered in the mathematical modelling of the reaction. For *o*-xylene oxidation, the mathematical modelling of results has been facilitated through information obtained from the previous quantitative study of the oxidation of *o*-tolualdehyde (an intermediate in *o*-xylene oxidation). Complete "rake" networks, leading to further knowledge of the relative importance of the different reaction steps, are proposed for both reactions.

EXPERIMENTAL

Experimental details, which have been described elsewhere (21), are summarized here.

Catalyst Preparation and Characterization

The catalyst, containing 1 w/w% of V_2O_5 supported on TiO_2 (anatase), was previously prepared by wet impregnation employing an aqueous solution of NH_4VO_3 in oxalic acid. The precursor was dried (12 h at 393 K) and calcined (4.5 h at 723 K).

The catalyst was characterized by XRD, LRS, FTIR, XPS, and TPR.

Kinetic Measurements

Reactions were carried out in a conventional flow apparatus at atmospheric pressure using a tubular reactor. Before each experiment, the catalyst was kept at 673 K, for 1 h, under flowing air, after which it was cooled to the reaction temperature. Kinetic results were obtained under steady state conditions, in the 533–633 K and 1.6×10^{-5}–2.3×10^{-4} $kg_{cat}\,dm^{-3}h$ ranges, organic reactant concentrations varying between 0.3 and 1.5 mol% in air.

MATHEMATICAL MODELLING

1. o-Tolualdehyde Oxidation

Previous kinetic studies of *o*-xylene oxidation (24) have shown that product selectivities depend simply on conversion of the reactant, and are almost independent of initial reactant concentrations except perhaps at the lowest O_2 pressures. It appears that, under all other conditions, surface reoxidation is faster than its reduction (19) and that therefore none of the steps involving O atoms is controlled by their availability. Their concentration therefore does not feature in the reaction schemes.

The reaction network of *o*-tolualdehyde oxidation is less complicated, with fewer species and reaction steps involved. Therefore, its mathematical modelling was first performed, expecting that the information obtained could be used in the analysis of *o*-xylene oxidation by facilitating calculation of kinetic parameters.

The reaction scheme proposed for *o*-tolualdehyde oxidation is shown in Scheme I. It consists of a "rake" mechanism

comprising a series of intermediate adsorbed species (T′, P′, PA′, and R′) that yield the observed products (phthalic anhydride (PA), phthalide (P), CO_2, and "residue" (R) (21)). The "residue," that, as was previously shown (21), does not act as precursor of selective oxidation products, can either stay on the catalyst surface or desorb and condense at the cooler parts of the system (21, 24, 25). Several routes for formation of CO_2 have been considered.

On the basis of Scheme I, the following rate equations can be written:

$$
\begin{aligned}
r_P &= K_d \Theta_{P'} - K_c P_P \\
r_{PA} &= K_f \Theta_{PA'} - K_e P_{PA} \\
r_R &= K_h \Theta_{R'} - k_g P_R \\
r_{CO_2} &= k_5 \Theta_{T'} + k_8 \Theta_{P'} + k_9 \Theta_{PA'} + k_{10} \Theta_{R'} \\
(-r_T) &= K_a P_T - K_b \Theta_{T'}
\end{aligned}
\tag{1}
$$

Mass balance equations for each adsorbed species lead to expressions that relate $\Theta_{T'}$, $\Theta_{P'}$, $\Theta_{PA'}$, and $\Theta_{R'}$ to P_T, P_P, P_{PA}, and P_R (see Appendix 1). Substituting such expressions in the above set and dividing all equations by $(-r_T)$ gives:

$$
\begin{aligned}
\frac{r_P}{(-r_T)} &= A - B \frac{P_P}{P_T} \\
\frac{r_{PA}}{(-r_T)} &= C + D \frac{P_P}{P_T} - E \frac{P_{PA}}{P_T} \\
\frac{r_R}{(-r_T)} &= F + G \frac{P_P}{P_T} + H \frac{P_{PA}}{P_T} - I \frac{P_R}{P_T} \\
\frac{r_{CO_2}}{(-r_T)} &= J + K \frac{P_P}{P_T} + L \frac{P_{PA}}{P_T} + M \frac{P_R}{P_T},
\end{aligned}
\tag{2}
$$

where $A, B, \ldots, M$ are constants depending on the adsorption–desorption and kinetic constants (see Appendix 2).

According to the one-dimensional plug flow model for a fixed-bed tubular reactor operating under isothermal
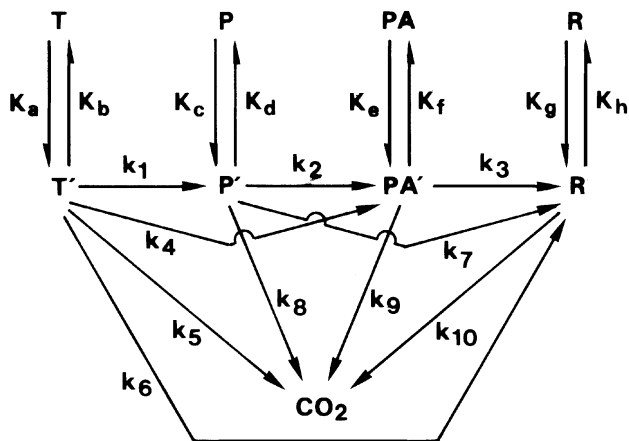
SCHEME I

$$y_P = X_1(z^B - z)$$

$$y_{PA} = z^E \left[X_2(z^{1-E} - 1) - X_3(z^{B-E} - 1) \right]$$

$$y_R = z^I \left[\frac{GX_1 - HX_2 - F}{1-I}\left(z^{1-I} - 1\right) + \frac{HX_3 - GX_1}{B-I}\left(z^{B-I} - 1\right) + \frac{H(X_2 - X_3)}{E-I}\left(z^{E-I} - 1\right) \right]$$

$$y_{CO_2} = 1 - z - y_P - y_{PA} - y_R$$

with $z = 1 - x$, $X_1 = \dfrac{A}{1-B}$, $X_2 = \dfrac{DX_1 - C}{1-E}$ and $X_3 = \dfrac{DX_1}{B-E}$

SCHEME II

conditions (28):

$$
\frac{r_i}{(-r_T)} = \frac{dy_i}{dx},
\tag{3}
$$

where y_i represents the yield of product i and x the conversion of reactant. On the other hand, by definition of yield and conversion

$$
\frac{P_i}{P_T} = \frac{y_i}{1-x},
\tag{4}
$$

with P_i representing the partial pressure of component i. Substituting Eqs. [3] and [4] in set [2], the following set is obtained:

$$
\begin{aligned}
\frac{dy_P}{dx} &= A - B \frac{y_P}{1-x} \\
\frac{dy_{PA}}{dx} &= C + D \frac{y_P}{1-x} - E \frac{y_{PA}}{1-x} \\
\frac{dy_R}{dx} &= F + G \frac{y_P}{1-x} + H \frac{y_{PA}}{1-x} - I \frac{y_R}{1-x} \\
\frac{dy_{CO_2}}{dx} &= 1 - \frac{dy_P}{dx} - \frac{dy_{PA}}{dx} - \frac{dy_R}{dx}.
\end{aligned}
\tag{5}
$$

Considering the initial conditions

$$
y_P = y_{PA} = y_R = y_{CO_2} = 0 \quad \text{at} \quad x = 0,
\tag{6}
$$

exact integration of the previous equations leads to those of Scheme II. The calculation of constants $A, B, \ldots, I$ was carried out, for each temperature, by nonlinear regression analysis, minimising the objective function

$$
\Phi = \sum_i \left[\frac{(y_i - y_i^c)}{y_i} \right]^2,
\tag{7}
$$

y_i^c being the values of yield calculated by means of equations of Scheme II. The following constraints were applied:

$$
A, B, \ldots, I \geq 0
\tag{8}
$$

$$
0 \leq y_i \leq 1 \quad \text{for} \quad x \in [0, 1].
\tag{9}
$$

TABLE 1

Oxidation of o-Tolualdehyde: Parameters Corresponding to Set [5]

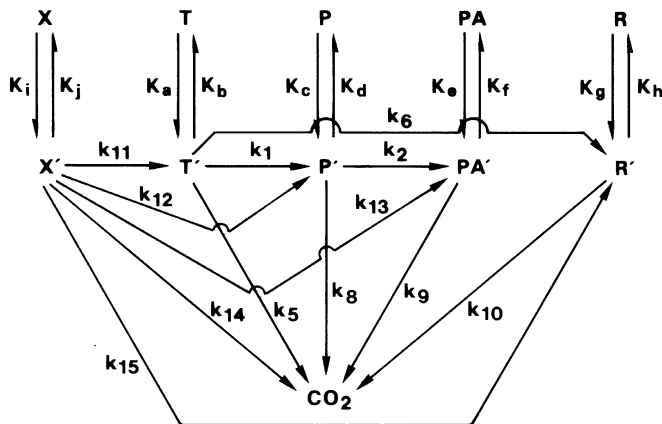| Parameters	Temperature (K)				
	533	573	593	613	633
A	0.22	0.21	0.15	0.09	0.27
B	3.00	1.26	0.89	0.56	2.33
C	0	0	0	0	0
D	8.65	7.96	8.45	7.37	5.90
E	0.10	0.49	0.39	0.14	0.01
F	0.68	0.80	0.90	0.93	0.65
G	0	0	0	0	0
H	0	0	0	0	0
I	1.82	4.51	3.77	1.43	1.78
r^a	0.995	0.976	0.977	0.993	0.997

[a] Correlation coefficient between experimental and calculated values of y_i.

The minimisation of the objective function was accomplished by using the Newton method as the search algorithm. Forward differencing was used for estimates of partial derivatives of the objective function, estimates of the variables in each step being obtained by quadratic extrapolation. The correlation between experimental and calculated yields was expressed in terms of the correlation coefficient (29).

The calculated parameters are presented in Table 1. The equations defining parameters A, B, ..., I in terms of the adsorption–desorption and kinetics constants are rather complex (see Appendix 2); however, it is noteworthy that for all temperatures the values corresponding to C, G, and H are zero. This provides the important evidence that steps 4, 7, and 3 can be neglected (see Appendix 2).

2. o-Xylene Oxidation

The reaction scheme considered for o-xylene oxidation is shown in Scheme III. In this case, o-tolualdehyde, phthalide, phthalic anhydride, CO_2, and "residue" were ob-

tained as reaction products (21). From the results obtained for o-tolualdehyde oxidation, steps 3, 4, and 7 have been suppressed and the rate equations can be written

$$r_T = K_b\Theta_{T'} - K_a P_T$$
$$r_P = K_d\Theta_{P'} - K_c P_P$$
$$r_{PA} = K_f\Theta_{PA'} - K_e P_{PA}$$
$$r_R = K_h\Theta_{R'} - K_g P_R$$
$$r_{CO_2} = k_{14}\Theta_{X'} + k_5\Theta_{T'} + k_8\Theta_{P'} + k_9\Theta_{PA'} + k_{10}\Theta_{R'}$$
$$(-r_X) = K_i P_X - k_j\Theta_{X'}.$$

[10]

Using a process similar to the one considered for o-tolualdehyde oxidation, set [11] is obtained (see Appendix 3)

$$\frac{dy_T}{dx} = A' - B'\frac{y_T}{1-x}$$
$$\frac{dy_P}{dx} = C' + D'\frac{y_T}{1-x} - E'\frac{y_P}{1-x}$$
$$\frac{dy_{PA}}{dx} = F' + G'\frac{y_T}{1-x} + H'\frac{y_P}{1-x} - I'\frac{y_{PA}}{1-x}$$
$$\frac{dy_R}{dx} = J' + K'\frac{y_T}{1-x} - L'\frac{y_R}{1-x}$$
$$\frac{dy_{CO_2}}{dx} = 1 - \frac{dy_T}{dx} - \frac{dy_P}{dx} - \frac{dy_{PA}}{dx} - \frac{dy_R}{dx},$$

[11]

where A', B', ..., L' are constants depending on the adsorption–desorption and kinetic constants (see Appendix 4). Using the initial conditions

$$y_T = y_P = y_{PA} = y_R = y_{CO_2} = 0 \quad \text{at} \quad x = 0 \quad [12]$$

exact integration of the equations of set (11) leads to those in Scheme IV. Parameters A', B', ..., L' have been determined as for o-tolualdehyde oxidation and the calculated values are given in Table 2. Again the equations defining A', B', ..., L' are complex (see Appendix 4), but for all temperatures C' and F' are zero showing that steps 12 and 13 can be neglected (see Appendix 4).

SCHEME III

$$y_T = X_1'(z^{B'} - z)$$

$$y_P = z^{E'}\left[X_2'(z^{1-E'} - 1) - X_3'(z^{B'-E'} - 1)\right]$$

$$y_{PA} = z^{I'}\left[\frac{G'X_1' - H'X_2' - F'}{1-I'}(z^{1-I'} - 1) + \frac{H'X_3' - G'X_1'}{B'-I'}(z^{B'-I'} - 1) + \frac{H'(X_2' - X_3')}{E'-I'}(z^{E'-I'} - 1)\right]$$

$$y_R = z^{L'}\left[\frac{K'X_1' - J'}{1-L'}\left(z^{1-L'} - 1\right) - \frac{K'X_1'}{B'-L'}\left(z^{B'-L'} - 1\right)\right]$$

$$y_{CO_2} = 1 - z - y_T - y_F - y_{PA} - y_R$$

with $z = 1 - x$, $X_1' = \dfrac{A'}{1-B'}$, $X_2' = \dfrac{D'X_1' - C'}{1-E'}$ and $X_3' = \dfrac{D'X_1'}{B'-E'}$

SCHEME IV

TABLE 2

Oxidation of *o*-Xylene: Parameters Corresponding to Set [11]

Parameters	Temperature (K)				
	533	573	593	613	633
A'	0.29	0.12	0.09	0.06	0.03
B	5.02	0.90	2.00	1.24	0.09
C	0	0	0	0	0
D	1.47	5.24	2.94	1.35	10.00
E	0.56	9.41	1.43	0.15	7.00
F	0	0	0	0	0
G	5.50	10.41	11.85	14.50	18.00
H	0.56	2.01	3.01	1.00	22.14
I	0	0.72	0.03	0.09	2.14
J	0.62	0.73	0.92	0.94	0.98
K'	1.92	1.64	0	0	0
L'	1.39	2.90	3.39	1.82	2.38
r^a	0.987	0.983	0.986	0.981	0.925

[a] Correlation coefficient between experimental and calculated values of y_i.

RESULTS AND DISCUSSION

Figures 1 and 2 show, for *o*-tolualdehyde and *o*-xylene oxidation respectively, the kinetic results for y_i as a function of conversion, and, as curves equations of sets [5] and [11] solved using the values of the parameters $A, \ldots, I$ and $A', \ldots, L'$ given in Tables 1 and 2; these parameters are complex functions of the kinetic and adsorption–desorption constants (see Appendices 2 and 4), and consequently no simple variation with temperature is expected.

Calculated y_i lines show different shapes for the two reactions, showing that the processes by which products are formed are not the same.

For *o*-tolualdehyde oxidation, no initial formation of PA was detected, its production involving a sequential mechanism. Parameter C shows that k_4 is zero (see Appendix 2), and that PA is not directly obtained from adsorbed *o*-tolualdehyde. Parameters G and H are also zero, showing that steps $P' \to R'$ and $PA' \to R'$ are not important (see Appendix 2), and that the "residue" is formed only through adsorbed *o*-tolualdehyde. The calculated y_R curves always exhibit a maximum, showing that the "residue" is converted into more oxidized products. Also, at higher conversions, PA is a source of CO_2 since, for such conditions, a maximum is generally found for y_{PA} curves. In fact, the slopes of y_{CO_2} curves continue to increase with the *o*-tolualdehyde conversion, showing that CO_2 is also formed from species such as *o*-tolualdehyde, phthalide, and phthalic anhydride.

For *o*-xylene oxidation, values of y_T and y_P are low, and good agreement between calculated and experimental values is observed. Constants C' and F' are always zero, so that, for the catalyst and experimental conditions used, steps

$X' \to P'$ and $X' \to PA'$ are negligible (see Appendix 4), PA' appears to be obtained only by the sequence $X' \to T' \to P'$. As PA is not a source of "residue" (as *o*-tolualdehyde oxidation has shown), and y_{PA} curves show generally a maximum, phthalic anhydride would act, under some experimental conditions, as a source of CO_2.

The initial slopes of y_R lines show that the formation of "residue" is involved in the first steps of the reaction network, X' and T' being important sources. As for *o*-tolualdehyde, the y_R curve always shows a maximum. As we have shown elsewhere (21), compounds deposited on the catalyst surface are not precursors of the selective oxidation products under these experimental conditions, but are intermediates that can suffer either desorption or complete oxidation to CO_2.

CONCLUSIONS

The proposed reaction networks have been shown to give a satisfactory description of results, and the use of the intermediate *o*-tolualdehyde as reactant has facilitated the mathematical treatment of the oxidation of *o*-xylene.

After adsorption of *o*-xylene on the catalyst surface, initiated by activation of a CH_3 side group (24, 30), reaction can proceed through (i) further selective oxidation of the adsorbed molecule, (ii) reaction between adsorbed molecules leading to the formation of "residue," or (iii) nonselective oxidation. The selective oxidation of *o*-xylene involves a sequential process, with formation of the desired product (PA), obtained from less oxidized adsorbed species. Mathematical modelling shows that PA cannot be obtained directly from *o*-xylene or *o*-tolualdehyde; thus adsorption of *o*-xylene involves hydrogen abstraction from one methyl group only, and the abstraction of hydrogen from two methyl groups simultaneously does not lead to selective oxidation. On the other hand, the formation of "residue," apparently mainly dimers (23), is associated with the first steps of the reaction scheme, *o*-xylene and *o*-tolualdehyde being the most important sources of such compounds. The nonoccurrence of dimerization of more oxidised species (e.g., P' and PA', that lead respectively to the formation of phthalide and phthalic anhydride in the gas phase) may be a consequence of the side-groups having been oxidised in whole or in part to carbonyl groups. Dimerization involves formation of a new bond between two C atoms (24), and this may perhaps only occur through methylene groups (23). On the other hand, for selective oxidation, the insertion of an O atom into the C–V bond is required (27) and a fast supply of O atoms to the catalyst surface is of extreme importance.

Reaction schemes used so far in mathematical modelling consider generally that CO_2 is obtained only from *o*-xylene (17, 19) or from *o*-xylene and PA (7–8). In the present study several routes for nonselective oxidation have been
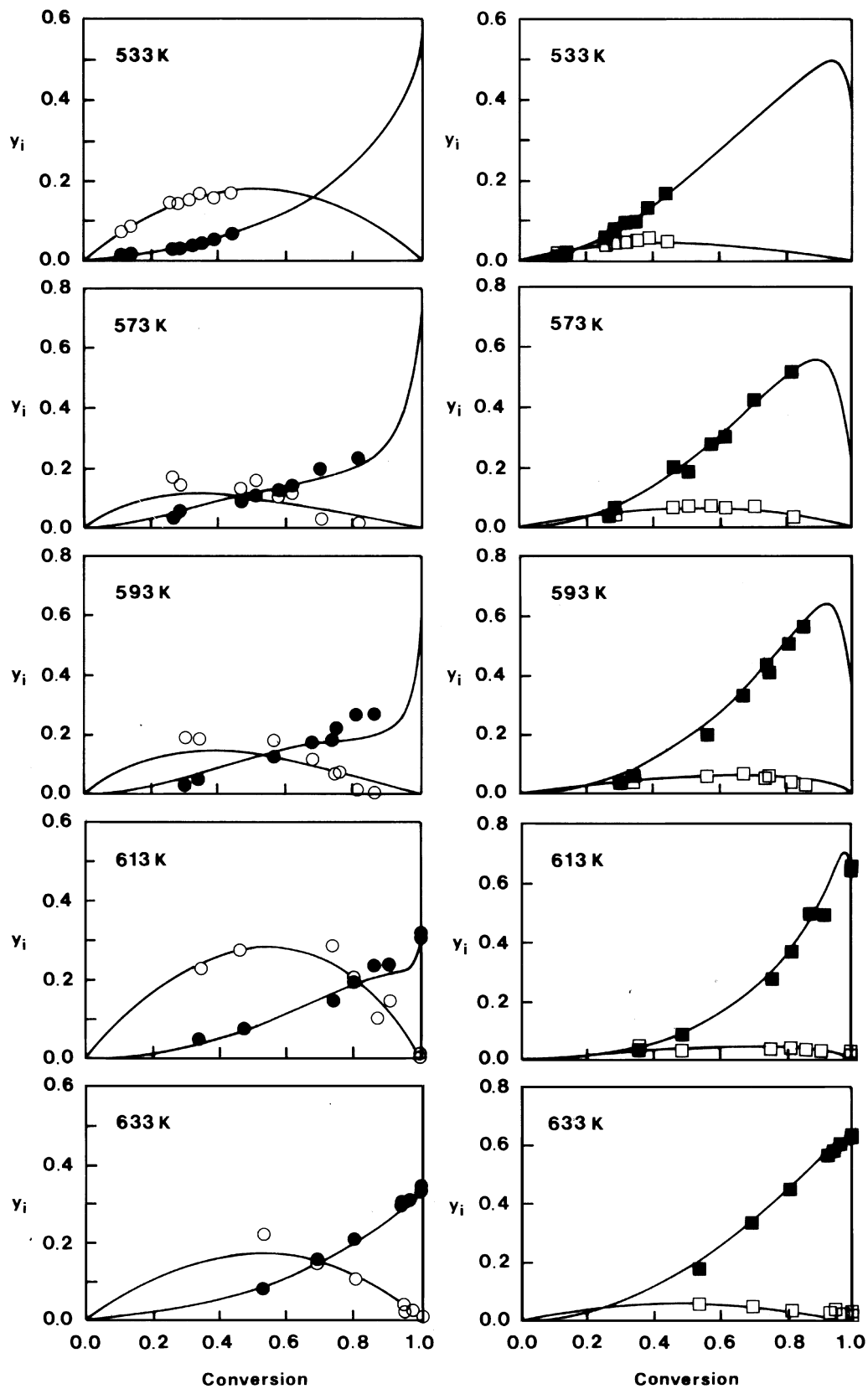
FIG. 1. Oxidation of o-tolualdehyde: yield (y_i) as a function of conversion, at different temperatures y_P, ($\square$); y_{PA}, ($\blacksquare$); y_R, ($\bigcirc$); y_{CO_2}, ($\bullet$). Curves calculated using equations of Scheme II and constants from Table 1.

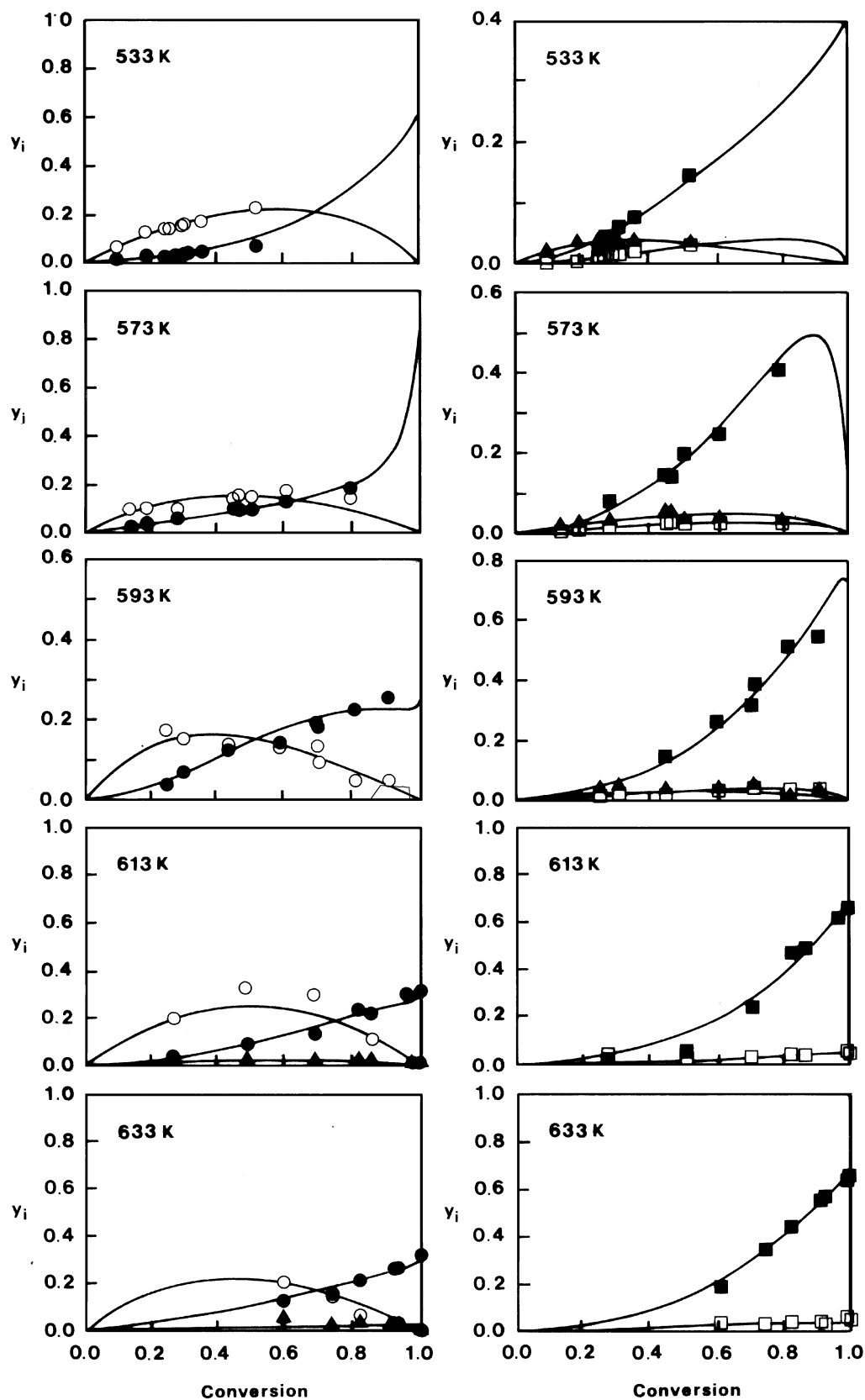**FIG. 2.** Oxidation of o-xylene: yield (y_i) as a function of conversion, at different temperatures. y_T, (▲); y_P, (□); y_{PA}, (■); y_R, (○); y_{CO_2}, (●). Curves calculated using equations of Scheme IV and constants from Table 2.

considered, and results point out that different species, including adsorbed *o*-xylene, adsorbed intermediates, phthalic anhydride, and "residue," can act as CO$_2$ sources, showing that its formation is associated with the adsorption of molecules on particularly strong active sites, different from those involved in selective oxidation. As pointed out elsewhere (21), the presence of strong Lewis acid sites can lead to a stronger interaction between aromatic molecules and the catalyst surface, enhancing the breaking of carbon–carbon bonds with the consequent formation of total combustion products.

APPENDIX 1

Mass Balance Equations of Adsorbed Species for *o*-Tolualdehyde Oxidation (Scheme I)

Considering Scheme I, T′, P′, PA′, and R′ are intermediate species; therefore, for steady state

$$\frac{d\Theta_{T'}}{dt} = 0 \qquad [A.1.1]$$

$$\frac{d\Theta_{P'}}{dt} = 0 \qquad [A.1.2]$$

$$\frac{d\Theta_{PA'}}{dt} = 0 \qquad [A.1.3]$$

$$\frac{d\Theta_{R'}}{dt} = 0. \qquad [A.1.4]$$

From Eq. [A.1.1]:

rate of formation of T′ = rate of consumption of T′
$$[A.1.5]$$

$$K_a P_T = (K_b + k_1 + k_4 + k_5 + k_6)\Theta_{T'} \qquad [A.1.6]$$

$$\Theta_{T'} = \alpha P_T \qquad [A.1.7]$$

with

$$\alpha = \frac{K_a}{K_b + k_1 + k_4 + k_5 + k_6}. \qquad [A.1.8]$$

From Eq. [A.1.2]:

rate of formation of P′ = rate of consumption of P′
$$[A.1.9]$$

$$k_1\Theta_{T'} + K_c P_P = (K_d + k_2 + k_7 + k_8)\Theta_{P'} \qquad [A.1.10]$$

$$\Theta_{P'} = \frac{k_1}{K_d + k_2 + k_7 + k_8}\Theta_{T'} + \frac{K_c}{K_d + k_2 + k_7 + k_8}P_P. \qquad [A.1.11]$$

Substituting Eq. [A.1.7] in [A.1.11]

$$\Theta_{P'} = \beta P_T + \gamma P_P \qquad [A.1.12]$$

with

$$\beta = \frac{k_1\alpha}{K_d + k_2 + k_7 + k_8} \qquad [A.1.13]$$

$$\gamma = \frac{K_c}{K_d + k_2 + k_7 + k_8}. \qquad [A.1.14]$$

From Eq. [A.1.3]:

rate of formation of PA′ = rate of consumption of PA′
$$[A.1.15]$$

$$k_4\Theta_{T'} + k_2\Theta_{P'} + K_e P_{PA} = (K_f + k_3 + k_9)\Theta_{PA'} \qquad [A.1.16]$$

$$\Theta_{PA'} = \frac{k_4}{K_f + k_3 + k_9}\Theta_{T'} + \frac{k_2}{K_f + k_3 + k_9}\Theta_{P'}$$

$$+ \frac{K_e}{K_f + k_3 + k_9}P_{PA}. \qquad [A.1.17]$$

Substituting Eq. [A.1.7] and [A.1.12] in [A.1.17]

$$\Theta_{PA'} = \delta P_T + \varepsilon P_P + \zeta P_{PA} \qquad [A.1.18]$$

with

$$\delta = \frac{k_4\alpha + k_2\beta}{K_f + k_3 + k_9} \qquad [A.1.19]$$

$$\varepsilon = \frac{k_2\gamma}{K_f + k_3 + k_9} \qquad [A.1.20]$$

$$\zeta = \frac{K_e}{K_f + k_3 + k_9}. \qquad [A.1.21]$$

From Eq. [A.1.4]:

rate of formation of R′ = rate of consumption of R′
$$[A.1.22]$$

$$K_g P_R + k_3\Theta_{PA'} + k_7\Theta_{P'} + k_6\Theta_{T'} = (K_h + k_{10})\Theta_{R'} \qquad [A.1.23]$$

$$\Theta_{R'} = \frac{k_6}{K_h + k_{10}}\Theta_{T'} + \frac{k_7}{K_h + k_{10}}\Theta_{P'}$$

$$+ \frac{k_3}{K_h + k_{10}}\Theta_{PA'} + \frac{K_g}{K_h + k_{10}}P_R. \qquad [A.1.24]$$

Substituting Eqs. [A.1.7], [A.1.12], and [A.1.18] in [A.1.24]

$$\Theta_{R'} = \eta P_T + \vartheta P_P + \iota P_{PA} + \kappa P_R \qquad [A.1.25]$$

with

$$\eta = \frac{k_6\alpha + k_7\beta + k_3\delta}{K_h + k_{10}} \qquad [A.1.26]$$

$$\vartheta = \frac{k_7\gamma + k_3\varepsilon}{K_h + k_{10}} \qquad [A.1.27]$$

$$\iota = \frac{k_3 \zeta}{K_h + k_{10}} \qquad [A.1.28]$$

$$\kappa = \frac{K_g}{K_h + k_{10}}. \qquad [A.1.29]$$

APPENDIX 2

Dependence of Constants A, B, . . ., M (Sets [2] and [5]) on Adsorption–Desorption and Kinetic Constants for o-Tolualdehyde Oxidation

$$A = \frac{K_d \beta}{K_a - K_b \alpha} = \frac{\alpha k_1 K_d}{(K_a - K_b \alpha)(K_d + k_2 + k_7 + k_8)} \qquad [A.2.1]$$

$$B = \frac{K_c - K_d \gamma}{K_a - K_b \alpha} = \frac{K_c(k_2 + k_7 + k_8)}{(K_a - K_b \alpha)(K_d + k_2 + k_7 + k_8)} \qquad [A.2.2]$$

$$C = \frac{K_f \delta}{K_a - K_b \alpha} = \frac{\alpha}{(K_a - K_b \alpha)} \frac{K_f}{(K_f + k_3 + k_9)}$$
$$\times \left(k_4 + \frac{k_1 k_2}{K_d + k_2 + k_7 + k_8} \right) \qquad [A.2.3]$$

$$D = \frac{K_f \varepsilon}{K_a - K_b \alpha} \qquad [A.2.4]$$

$$E = \frac{K_e - K_f \zeta}{K_a - K_b \alpha} = \frac{K_e(k_3 + k_9)}{(K_a - K_b \alpha)(K_f + k_3 + k_9)} \qquad [A.2.5]$$

$$F = \frac{K_h \eta}{K_a - K_b \alpha} = \frac{K_h}{(K_a - K_b \alpha)(K_h + k_{10})}$$
$$\times \left(k_6 \alpha + \frac{k_7 k_1 \alpha}{K_d + k_2 + k_7 + k_8} + \frac{k_3(k_4 \alpha + k_2 \beta)}{K_f + k_3 + k_9} \right) \qquad [A.2.6]$$

$$G = \frac{K_h \vartheta}{K_a - K_b \alpha}$$
$$= \frac{K_c K_h}{(K_d + k_2 + k_7 + k_8)(K_a - K_b \alpha)(K_h + k_{10})}$$
$$\times \left(k_7 + \frac{k_2 k_3}{K_f + k_3 + k_9} \right) \qquad [A.2.7]$$

$$H = \frac{K_h \iota}{K_a - K_b \alpha} = \frac{K_h}{(K_a - K_b \alpha)} \frac{\zeta}{(K_h + k_{10})} k_3 \qquad [A.2.8]$$

$$I = \frac{K_g - K_h \kappa}{K_a - K_b \alpha} = \frac{K_g k_{10}}{(K_a - K_b \alpha)(K_h + k_{10})} \qquad [A.2.9]$$

$$J = 1 - A - C - F \qquad [A.2.10]$$

$$K = B - D - G \qquad [A.2.11]$$

$$L = E - H \qquad [A.2.12]$$

$$M = I \qquad [A.2.13]$$

with $\alpha, \beta, \ldots, \kappa$ as defined in Appendix 1. Since parameters C, G, and H are zero it can be concluded from Eqs. [A.2.3], [A.2.7], and [A.2.8] that k_4, k_7, and k_3 are zero. In fact, in Eq. [A.2.3] parameters α and K_f are not zero (they are also included in Eqs. [A.2.1] and A.2.4, respectively, that define parameters A and B, which are never zero), meaning that the term

$$\left(k_4 + \frac{k_1 k_2}{K_d + k_2 + k_7 + k_8} \right)$$

is zero, thus k_4 is zero and $K_d + k_2 + k_7 + k_8 \gg k_1 k_2$. Similar conclusions, concerning k_7 and k_3, can be obtained from Eqs. [A.2.7] and [A.2.8], respectively.

APPENDIX 3

Mass Balance Equations of Adsorbed Species for o-Xylene Oxidation (Scheme II)

Considering Scheme II, X′, T′, P′, PA′, and R′ are intermediate species, therefore, for steady state

$$\frac{d\Theta_{X'}}{dt} = 0 \qquad [A.3.1]$$

$$\frac{d\Theta_{T'}}{dt} = 0 \qquad [A.3.2]$$

$$\frac{d\Theta_{P'}}{dt} = 0 \qquad [A.3.3]$$

$$\frac{d\Theta_{PA'}}{dt} = 0 \qquad [A.3.4]$$

$$\frac{d\Theta_{R'}}{dt} = 0. \qquad [A.3.5]$$

From Eq. [A.3.1]:

rate of formation of X′ = rate of consumption of X′ [A.3.6]

$$K_i P_X = (K_j + k_{11} + k_{12} + k_{13} + k_{14} + k_{15})\Theta_{X'} \qquad [A.3.7]$$

$$\Theta_{X'} = \alpha' P_X \qquad [A.3.8]$$

with

$$\alpha' = \frac{K_i}{K_j + k_{11} + k_{12} + k_{13} + k_{14} + k_{15}}. \qquad [A.3.9]$$

From Eq. [A.3.2]:

rate of formation of T′ = rate of consumption of T′ [A.3.10]

$$K_a P_T + k_{11}\Theta_{X'} = (K_b + k_1 + k_5 + k_6)\Theta_{T'} \qquad [A.3.11]$$

$$\Theta_{T'} = \frac{k_{11}}{K_b + k_1 + k_5 + k_6}\Theta_{X'} + \frac{K_a}{K_b + k_1 + k_5 + k_6}P_T. \quad [A.3.12]$$

Substituting Eq. [A.3.8] in Eq. [A.3.12],

$$\Theta_{T'} = \beta' P_X + \gamma' P_T \quad [A.3.13]$$

with

$$\beta' = \frac{k_{11}\alpha'}{K_b + k_1 + k_5 + k_6} \quad [A.3.14]$$

$$\gamma' = \frac{K_a}{K_b + k_1 + k_5 + k_6}. \quad [A.3.15]$$

From Eq. [A.3.3]:

rate of formation of P' = rate of consumption of P' [A.3.16]

$$K_c P_P + k_1\Theta_{T'} + k_{12}\Theta_{X'} = (K_d + k_2 + k_8)\Theta_{P'} \quad [A.3.17]$$

$$\Theta_{P'} = \frac{k_{12}}{K_d + k_2 + k_8}\Theta_{X'} + \frac{k_1}{K_d + k_2 + k_8}\Theta_{T'}$$
$$+ \frac{K_c}{K_d + k_2 + k_8}P_P. \quad [A.3.18]$$

Substituting Eqs. [A.3.8] and [A.3.13] in Eq. [A.3.18],

$$\Theta_{P'} = \delta' P_X + \varepsilon' P_T + \zeta' P_P \quad [A.3.19]$$

with

$$\delta' = \frac{k_{12}\alpha'}{K_d + k_2 + k_8} + \frac{k_1\beta'}{K_d + k_2 + k_8} \quad [A.3.20]$$

$$\varepsilon' = \frac{k_1\gamma'}{K_d + k_2 + k_8} \quad [A.3.21]$$

$$\zeta' = \frac{K_c}{K_d + k_2 + k_8}. \quad [A.3.22]$$

From Eq. [A.3.4]:

rate of formation of PA' = rate of consumption of PA' [A.3.23]

$$K_e P_{PA} + k_2\Theta_{P'} + k_{13}\Theta_{X'} = (K_f + k_9)\Theta_{PA'} \quad [A.3.24]$$

$$\Theta_{PA'} = \frac{k_{13}}{K_f + k_9}\Theta_{X'} + \frac{k_2}{K_f + k_9}\Theta_{P'} + \frac{K_e}{K_f + k_9}P_{PA}. \quad [A.3.25]$$

Substituting Eqs. [A.3.8], [A.3.13], and [A.3.19] in Eq. [A.3.25],

$$\Theta_{PA'} = \eta' P_X + \vartheta' P_T + \iota' P_P + \kappa' P_{PA} \quad [A.3.26]$$

with

$$\eta' = \frac{k_{13}\alpha'}{K_f + k_9} + \frac{k_2\delta'}{K_f + k_9} \quad [A.3.27]$$

$$\vartheta' = \frac{k_2\varepsilon'}{K_f + k_9} \quad [A.3.28]$$

$$\iota' = \frac{k_2\zeta'}{K_f + k_9} \quad [A.3.29]$$

$$\kappa' = \frac{K_e}{K_f + k_9}. \quad [A.3.30]$$

From Eq. [A.3.5]:

rate of formation of R' = rate of consumption of R' [A.3.31]

$$K_g P_R + k_6\Theta_{T'} + k_{15}\Theta_{X'} = (K_h + k_{10})\Theta_{R'} \quad [A.3.32]$$

$$\Theta_{R'} = \frac{k_{15}}{K_h + k_{10}}\Theta_{X'} + \frac{k_6}{K_h + k_{10}}\Theta_{T'} + \frac{K_g}{K_h + k_{10}}P_R. \quad [A.3.33]$$

Substituting Eqs. [A.3.8] and [A.3.13] in [A.3.33],

$$\Theta_{R'} = \lambda' P_X + \mu' P_T + \nu' P_R \quad [A.3.34]$$

with

$$\lambda' = \frac{k_{15}\alpha'}{K_h + k_{10}} + \frac{k_6\beta'}{K_h + k_{10}} \quad [A.3.35]$$

$$\mu' = \frac{k_6\gamma'}{K_h + k_{10}} \quad [A.3.36]$$

$$\nu' = \frac{K_g}{K_h + k_{10}}. \quad [A.3.37]$$

APPENDIX 4

Dependence of Constants $A', B', \dots, L'$ (set [11]) on Adsorption–Desorption and Kinetic Constants for o-Xylene Oxidation

$$A' = \frac{K_b\beta'}{K_i - K_j\alpha'} = \frac{K_b k_{11}\alpha'}{(K_i - K_j\alpha')(K_b + k_1 + k_5 + k_6)} \quad [A.4.1]$$

$$B' = \frac{K_a - K_b\gamma'}{K_i - K_j\alpha'} = \frac{K_a(k_1 + k_5 + k_6)}{(K_i - K_j\alpha')(K_b + k_1 + k_5 + k_6)} \quad [A.4.2]$$

$$C' = \frac{K_d\delta'}{K_i - K_j\alpha'} = \frac{\alpha'}{(K_i - K_j\alpha')}\frac{K_d}{(K_d + k_2 + k_8)}$$
$$\times \left(k_{12} + \frac{k_1 k_{11}}{K_b + k_1 + k_5 + k_6} \right) \quad [A.4.3]$$

$$D' = \frac{K_d\varepsilon'}{K_i - K_j\alpha'} \quad [A.4.4]$$

$$E' = \frac{K_c - K_d \zeta'}{K_i - K_j \alpha'} = \frac{K_c(k_2 + k_8)}{(K_i - K_j \alpha')(K_d + k_2 + k_8)} \quad \text{[A.4.5]}$$

$$F' = \frac{K_f \eta'}{K_i - K_j \alpha'}$$

$$= \frac{\alpha'}{(K_i - K_j \alpha')} \frac{K_f}{(K_f + k_9)} \left(k_{13} + \frac{k_2 k_{12}}{K_d + k_2 + k_8} \right.$$

$$\left. + \frac{k_1 k_2 k_{11}}{(K_d + k_2 + k_8)(K_b + k_1 + k_5 + k_6)} \right) \quad \text{[A.4.6]}$$

$$G' = \frac{K_f \vartheta'}{K_i - K_j \alpha'} = \frac{K_f}{(K_i - K_j \alpha')} \frac{\varepsilon'}{(K_f + k_9)} k_2 \quad \text{[A.4.7]}$$

$$H' = \frac{K_f \iota'}{K_i - K_j \alpha'} = \frac{K_f}{(K_i - K_j \alpha')} \frac{\zeta'}{(K_f + k_9)} k_2 \quad \text{[A.4.8]}$$

$$I' = \frac{K_e - \kappa' K_f}{K_i - K_j \alpha'} = \frac{K_e k_9}{(K_i - K_j \alpha')(K_f + k_9)} \quad \text{[A.4.9]}$$

$$J' = \frac{K_h \lambda'}{K_i - K_j \alpha'} \quad \text{[A.4.10]}$$

$$K' = \frac{K_h \mu'}{K_i - K_j \alpha'} \quad \text{[A.4.11]}$$

$$L' = \frac{K_g - K_h \nu'}{K_i - K_j \alpha'} = \frac{K_g k_{10}}{(K_i - K_j \alpha')(K_h + k_{10})} \quad \text{[A.4.12]}$$

with $\alpha', \beta', \ldots, \nu'$ defined in Appendix 3. Since parameters C and F' are zero it can be concluded from Eqs. [A.4.3] and [A.4.6] that k_{12} and k_{13}, respectively, are negligible. In fact, in Eq. [A.4.3], α' and K_d are not zero (such variables are also included in Eqs. [A.4.1] and [A.4.4] that define parameters A' and D' which are never zero), meaning that the term $(k_{12} + (k_1 k_{11}/K_b + k_1 + k_5 + k_6))$ is zero; i.e., k_{12} is negligible and $K_b + k_1 + k_5 + k_6 \gg k_1 k_{11}$. As for Eq. [A.4.6], K_f is not zero since parameters G' and H', obtained from Eqs. [A.4.7] and [A.4.8], respectively, (where K_f is included) are never zero; thus the term $(k_{13} + (k_2 k_{12}/K_d + k_2 + k_8) + (k_1 k_2 k_{11}/(K_d + k_2 + k_8)(K_b + k_1 + k_5 + k_6)))$ is zero, showing that k_{13} is negligible.

APPENDIX 5

Nomenclature

k_i	$i = 1, 2, \ldots, 15$ kinetic constants
K_i	$i = a, b, \ldots, j$ adsorption and desorption constants
n	number of experimental y_i values
P	gas-phase phthalide
P$'$	adsorbed phthalide
P_i	partial pressure of component i
PA	gas-phase phthalic anhydride
PA$'$	adsorbed phthalic anhydride
R	"residue" either desorbed or adsorbed over the catalytic surface
R$'$	adsorbed molecules, precursors of "residue"
r_i	formation rate of product i
$(-r_i)$	reaction rate of reactant i
S_i	product i selectivity, moles of product (or for CO_2, mol/8) per mole of reactant converted
T	gas-phase o-tolualdehyde
T$'$	adsorbed o-tolualdehyde
T_R	reaction temperature
X	gas-phase o-xylene
X$'$	adsorbed o-xylene
x	conversion of reactant
y_i	component i yield
y_i^c	yield of component i calculated
z	$1 - x$
$\alpha, \beta, \ldots, \kappa$	constants depending on kinetic and adsorption–desorption constants
$\alpha', \beta', \ldots, \nu'$	constants depending on kinetic and adsorption–desorption constants
Θ_i	surface concentration of component i

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