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The Kinetics of the Vapor-Phase Oxidation of o-Xylene over a Vanadium Oxide Catalyst

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The rate of oxidation of *o*-xylene was studied in a differential bed reactor over the following ranges of conditions: 290 to 310°C, (0.5 to 3.0) × 10^{-4} g-mole *o*-xylene/l, (5 to 100) × 10^{-4} g-mole oxygen/l. The catalyst used was a vanadium oxide/potassium sulfate-promoted/silica, which had been used in previous kinetic studies.

The data provide further support for the steady-state adsorption model proposed previously to describe the oxidation of naphthalene, toluene, and benzene. Particular attention was paid to the low oxygen concentration region, but no evidence was found to support the second order model proposed by Ioffe and Lyubarskii.

INTRODUCTION

Beginning with the work of Calderbank on naphthalene in 1952 (*1*), several studies have been reported in the literature which have the common aim of establishing a technological basis for the industrially important oxidation processes carried out over vanadium catalysts. The rates of oxidation of the main industrial raw materials have been determined, viz. naphthalene, benzene, and more recently *o*-xylene, and the rate data have been interpreted by a variety of kinetic models.

Two models now appear to be gathering support, either directly or in slightly modified form. These are the steady-state oxidation-reduction model proposed by Mars and van Krevelen (*2*) and the steady-state adsorption model proposed by Shelstad, Downie, and Graydon (*3*). Since the catalyst is known to reach a steady-state composition with a range of vanadium valency states (*4*) and since chemisorption of oxygen is involved in the adsorption model, it may be impossible to distinguish between them. They both yield the same rate equation, and hence support for one kinetically is also support for the other.

There has been a certain amount of confusion over the assumptions of the models, and this has led to modifications being proposed and to spurious distinctions being made. For example, Vrbaski (*5*) appears to be confused on the point that the first order dependence on oxygen and on the hydrocarbon is assumed *in the development of the adsorption model,* but this does *not* mean that the resulting equation is first order in the reactants. In fact, the rate equation is "changing order" in the reactants. It is possible that Vrbaski's modification of the model is therefore unnecessary. Another example of minor confusion is in the work of Bhattacharyya *et al.* (*6*) in which a distinction between the models is made by saying that the hydrocarbon is chemisorbed in the Mars and van Krevelen model and not in the other model. In fact the hydrocarbon is assumed to behave in the same way in both models; i.e., Mars and van Krevelen's adsorption is equivalent to collision with the "oxidized" surface.

The supporting evidence is accumulating, but it should be noted that a number of weak assumptions have been made in data

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interpretation. Mars and van Krevelen had to assume that their small fluidized bed reactor behaved as an ideal plug flow reactor for analysis. They also assumed that the integrated form of the rate equation could be obtained directly from the differential form and used with high conversion rate data to test the model. This is only true in the special case where series reactions do not occur to a significant extent. Otherwise, the reaction of intermediates must be included in the steady-state equation, since these reactions contribute to the disappearance of oxygen from the surface by chemical reaction. The rate equation when series reactions are considered becomes

$$-r_{\mathrm{R1}} = \frac{k_a k_{r1} C_o C_{\mathrm{R1}}}{k_a C_o + \Sigma_i n_i k_{ri} C_{\mathrm{R}i}}. \qquad (1)$$

This equation does not give the integral form used by Mars and van Krevelen. In a recent paper, Herten and Froment (*7*) tested the Mars and van Krevelen Model by using high conversion data for the oxidation of *o*-xylene. This oxidation involves a number of series reactions, and therefore Herten and Froment's treatment using the integrated form of the initial rate equation does not appear to be valid. Another type of difficulty arises in assessing the support for the adsorption model offered by Vrbaski (*5*) based on data reported by Vrbaski and Mathews (*8*). The reaction rate is plotted against the initial concentration of reactant despite the high conversions involved. The differential form of the rate equation appears to have been used to interpret integral data.

The present work concludes a series of studies carried out using a catalyst from a single batch (*3, 9, 10, 11, 12*). The difficulties noted above have been avoided by using a differential bed reactor and conducting an initial rate study. New data are presented on the oxidation of *o*-xylene. The complete set of data on this catalyst are interpreted by the steady-state adsorption model. However, as stated above, the support offered applies equally well to the steady-state oxidation-reduction model.

NOMENCLATURE

A = Arrhenius frequency factor
C_o = concentration of oxygen, moles/liter
C_{R} = concentration of hydrocarbon, moles/liter
E = activation energy, cal/mole
k_a = specific rate of oxygen adsorption, liter/g catalyst sec (in Model 1)
K_a = oxygen equilibrium adsorption constant
k_d = specific rate of oxygen desorption, liter/g catalyst sec
k_r = reaction rate constant, liter/g catalyst sec
K_{R} = hydrocarbon equilibrium adsorption constant
n = stoichiometric number, moles oxygen required/mole hydrocarbon reacted
R = gas constant, cal/g-mole °K
r_{R} = rate of hydrocarbon reaction, moles/g catalyst sec
T = temperature, °K
β = Mars and van Krevelen's stoichiometric number (*2*), moles oxygen required/moles hydrocarbon reacted
i = subscript denoting an intermediate in the series reaction of R to products

EXPERIMENTAL

A differential bed reactor was used in the present study to facilitate the analysis of the results. Reaction rates of *o*-xylene were determined as a function of oxygen and *o*-xylene concentration for three temperatures.

The apparatus used was similar to that of previous investigators (*9, 13*); where there are minor differences, they are noted below. Capillary resistance flowmeters were used to measure nitrogen and oxygen flows. The concentration of *o*-xylene was determined by the temperature of the water bath and the amount of nitrogen metered through the carburetor containing *o*-xylene. The reactants were preheated prior to entering the reactor.

The reactor consisted of an 8- by ¾-in.-diameter stainless steel 304 tube. This tube was encased in a split aluminum block heated by four cartridge heaters embedded in the block. The aluminum thus provided uniform heating to the reactor. This design permitted reactor tubes of different materials to be tested in the system. The stainless steel 304 reactor was found to be superior to either glass or aluminum in the reduction of blank reactions. The catalyst was supported in the reactor tube on a stainless steel screen. Temperature was controlled by a thermocouple touching the reactor wall adjacent to the catalyst bed. The temperatures of the inlet and outlet gases were measured by thermocouples inserted into these streams. The reaction products were collected in glass traps immersed in Dry Ice. The effluent from the traps was fed directly into the gas chromatograph for carbon dioxide analysis.

Details of the catalyst used have been reported elsewhere (*3*). The catalyst is a sample of the potassium sulfate-promoted vanadium pentoxide on silica carrier catalyst used in previous studies (*3, 9, 10, 11, 12*). The surface area is 52 m^2/g.

PROCEDURE

After the reactor, carburetor, constant temperature bath, and preheating line had attained their operating temperatures, the oxygen and nitrogen flows were adjusted to give predetermined concentrations for the run. Approximately 2 hr were allowed for the system to achieve steady-state conditions before starting a run. Tests showed that the period of unsteady-state operation was less than 1 hr.

The product was collected in the Dry Ice traps for periods ranging ½ to 2 hr. During the run, the exit gases from the traps were periodically analyzed for carbon dioxide by gas chromatography. The analysis was carried out on a 10-ft Poropak-Q column operated isothermally at room temperature. At the end of a run, the product was weighed and then diluted to a standard volume. This solution was analyzed quantitatively for *o*-tolualdehyde and *p*-benzoquinone.

o-Tolualdehyde analysis was carried out on an 8-ft, 6% silicone gum rubber SE-52 on 60/80 diatoport S column. The column was temperature programmed from 75°C at 10°C per minute to give good separation of *o*-tolualdehyde from *o*-xylene and *p*-benzoquinone. Peak areas were used for calibration purposes and subsequent quantitative determinations of both *o*-tolualdehyde and carbon dioxide.

Analysis for *p*-benzoquinone was by absorbance measurements on a spectrophotometer. Measurements were made at 450, 460, and 470 mμ.

The products found in the present study, with the approximate percentages of *o*-xylene reacted to each, were:

80% to *o*-tolualdehyde
12% to *p*-benzoquinone
8% to carbon dioxide
trace to carbon monoxide.

The product distribution remained essentially constant over the range of conditions studied. The average value of the stoichiometric number, *n*, was 2.13.

The products reported were identified by retention time on various columns in conjunction with chemical analysis. Some doubt existed as to whether the *o*-tolualdehyde peak might be composed of *o*-tolualdehyde and *o*-xylene oxide (*13*). Through repeated extractions of the product solution with 2,2′dinitrophenylhydrazine, the '*o*-tolualdehyde peak' was removed from a chromatogram of the solution (*14*). Since *o*-xylene oxide does not react with 2,2′dinitrophenylhydrazine, it was concluded that the peak did not contain *o*-xylene oxide.

The range of concentrations and temperatures at which the present work was carried out is shown in Table 1.

TABLE 1
REACTION CONDITIONS

Reactor temperature (°C)	Oxygen concn (moles/l) × 10^4	*o*-Xylene concn (moles/l) × 10^4
290	50	0.5–3.0
300	50	0.5–3.0
310	50	0.5–3.0
290	10–100	2
300	5–100	2
310	10–100	2

RESULTS

Certain factors may obscure reaction rate data obtained for gas/solid catalytic reactions. The effect of these factors must be reduced to a level of insignificance by the choice of conditions, or corrections to the rate data must be made. The factors considered in the present study were the influence of a blank reaction, catalyst aging, and diffusion resistance.

A thorough examination was made of the temperature limits at which a noncatalytic or blank reaction becomes significant. It was found that at temperatures below 315°C this reaction would be insignificant. Similar studies on a glass reactor revealed that at temperatures of 310°C the blank reaction was large enough to obscure any rate data on the catalyst. The present work was carried out in a 304 stainless steel reactor at temperatures from 290 to 310°C.

In order to obtain a meaningful and consistent set of data on a catalyst, experimental runs should be carried out on a catalyst of constant activity. As the catalyst is on stream, however, its activity decreases and it becomes necessary to correct reactions to some constant catalyst age. In order to determine the aging characteristics of the catalyst, various standard runs were periodically performed. These runs showed that there was a slow decline in activity over a period of 500 hr and that the aging behavior was essentially the same for different temperatures and reactant concentrations. The rate data were corrected to a standard catalyst age of 200 hr. This correction was less than ±10% of the uncorrected rate in all cases.

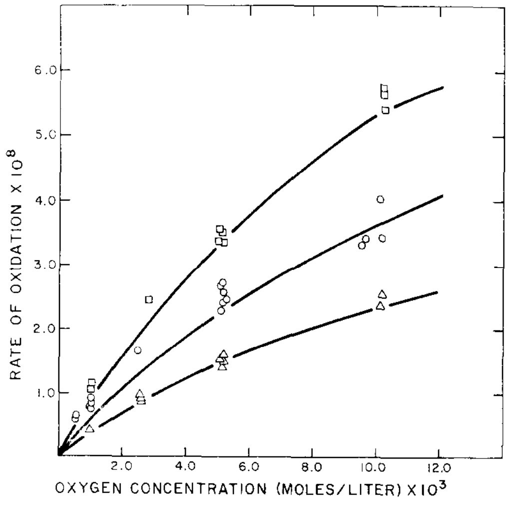

FIG. 1. Rate of oxidation of *o*-xylene (moles/g of catalyst/sec) as a function of oxygen concentration; *o*-xylene concentration = 2×10^{-4} mole/l. □, 310°C; ○, 300°C; △, 290°C.

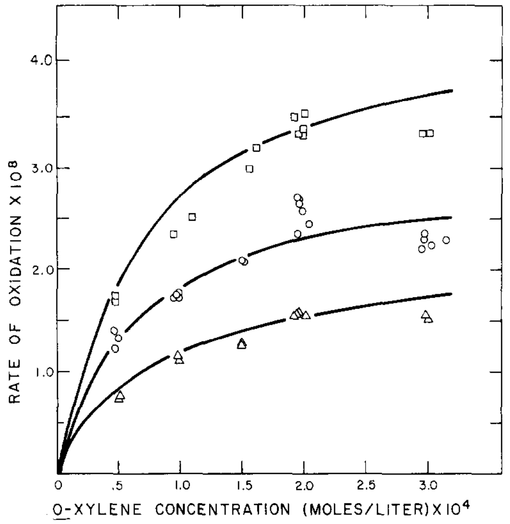

FIG. 2. Rate of oxidation of *o*-xylene (moles/g of catalyst/sec) as a function of *o*-xylene concentration; oxygen concentration = 50×10^{-4} mole/l. □, 310°C; ○, 300°C; △, 290°C.

Calculations were made to determine the effects of diffusion resistance. These calculations showed that at the rate of reaction and conditions encountered in the study the effects of both external and pore diffusion were not significant.

Figure 1 shows the rate of *o*-xylene reaction as a function of oxygen concentration for temperatures of 290, 300, and 310°C. The *o*-xylene concentration was approximately constant at 2.0×10^{-4} mole/l. In Fig. 2, the reaction rates are shown as a function of *o*-xylene concentration with oxygen concentration constant at 50.0×10^{-4} mole/l. The range of reaction rates shown gave conversions of *o*-xylene from 0.5 to 6.3 mole %.

DISCUSSION

The changing order form of the reaction rate data shown in Figs. 1 and 2 suggests

TABLE 2
Summary of Reaction Rate Models Tested

Model	Assumptions	Rate equation for initial rate conditions
1	A steady-state adsorption model (SSAM)—a steady state is assumed between the rate of adsorption of oxygen on the surface and the rate of removal of oxygen by reaction with R from the gas phase	$r_R = \dfrac{k_a k_r C_o C_R}{k_a C_o + n k_r C_R}$
2	SSAM—additional assumption to Model 1 is made that oxygen dissociates	$r_R = \dfrac{k_a k_r C_R (C_o)^{1/2}}{k_a (C_o)^{1/2} + n k_r C_R}$
3	SSAM—additional assumption to Model 1 is made that the oxygen desorption rate is not negligible	$r_R = \dfrac{k_a k_r C_o C_R}{k_d + k_a C_o + n k_r C_R}$
4	Rideal mechanism—equilibrium concentration of oxygen is assumed established on the surface, with reaction occurring between adsorbed oxygen and gas phase hydrocarbon	$r_R = \dfrac{k_r K_A C_o C_R}{1 + K_A C_o}$
5	Langmuir-Hinshelwood model—equilibrium concentrations of oxygen and hydrocarbon are assumed established on the surface, with reaction occurring between adsorbed reactants	$r_R = \dfrac{k_r K_A K_R C_o C_R}{(1 + K_A C_o + K_R C_R)^2}$

various possible kinetic models to describe the data. Five different models were tested on *o*-xylene, benzene (*12*), and toluene (*9*) data on the same catalyst. The models tested are summarized in Table 2, which shows the main assumptions involved and the resulting rate equations.

The development of the steady-state adsorption model has been fully described previously (*3, 9*). The resulting rate equations for Model 2 and Model 3 follow in a similar manner to the development of Model 1. In Model 2, with dissociation of oxygen considered, the adsorption step has been assumed to involve the interaction of a single surface site and an atom of oxygen. This does not seem to be a particularly practical case, but it has been used and is included here for interest. Consideration was given to the more interesting case in which interaction occurs between molecular oxygen and two adjacent surface sites, resulting in oxygen dissociation on the surface. The resulting rate equation, however, did not conform to the changing order behavior of the data and was rejected on this basis. Models 4 and 5 are the familiar Rideal and Langmuir-Hinshelwood rate expressions obtained when equilibrium adsorption of reactant is assumed. All models are restricted to initial rate conditions.

Three criteria are available for discrimination among these models:

(1) The rate equation for the model should correlate the data.

(2) Values of the rate parameters for a particular hydrocarbon should be capable of correlation on an Arrhenius plot.

(3) For models based on the assumption of a steady state between adsorption of oxygen onto the catalyst surface and reaction with gas phase hydrocarbon, a third criterion should be satisfied. Values of k_a obtained at various temperatures and for various hydrocarbons should correlate on an Arrhenius plot, and an activation energy of adsorption describing the chemisorption of oxygen on a particular catalyst lattice should result.

Data on *o*-xylene, benzene (*12*), and toluene (*9*) were correlated by nonlinear least squares regression analysis. The resulting correlations and rate parameters obtained for the five models were then examined in terms of the criteria given above. The results for these tests are summarized in Table 3.

In general, values of rate constants and equilibrium constants were scattered, with no specific trends for any of these models. Values of k_d, the desorption rate constant in Model 3, were negative in certain cases. Discrimination between Models 1 and 2 was on the basis of criterion 3. Values of k_a in Model 2 for different hydrocarbon

TABLE 3
SUMMARY OF WORK DONE ON MODEL DISCRIMINATION[a]

Model	Criterion 1	Criterion 2	Criterion 3
1	√	√	√
2	√	√	×
3	√	×	×
4	×	×	
5	√	×	

[a] √—satisfies criterion
×—does not satisfy criterion.

Model 1 provided the best correlation of the data, criterion 1, although a distinction between the models on this basis could not be made. The correlation provided by Model 4 was, however, definitely not as good as for any of the other models. Rate parameters obtained for Models 3, 4, and 5 failed to satisfy criterion 2 since the rate parameters obtained provided no meaningful correlations on Arrhenius-type plots.

systems failed to correlate on an Arrhenius-type plot, although values of rate parameters for a specific hydrocarbon did correlate on such a plot. Thus of the models tested, Model 1 provided the best description of the data on the basis of the criteria.

The results for Model 1 are summarized in Table 4, which shows k_a and k_r values for naphthalene, toluene, benzene, and *o*-xylene on the same catalyst. The values of k_a and k_r obtained for *o*-xylene, as shown in Fig. 3, are well correlated in the temperature range 290 to 310°C by the Arrhenius relationships,

$$\ln k_a = 11.8 - 26{,}000/RT$$
$$\ln k_r = 16.8 - 28{,}000/RT$$

TABLE 4
RATE CONSTANTS FOR MODEL 1

Hydrocarbon	Temp. (°C)	k_a	k_r
Naphthalene	312	1.81×10^{-5}	5.40×10^{-3}
(*3*)	335	6.17×10^{-5}	7.85×10^{-3}
Toluene	300	1.11×10^{-5}	5.24×10^{-5}
(*9*)	325	5.59×10^{-5}	1.18×10^{-4}
	350	1.58×10^{-4}	2.38×10^{-4}
Benzene	350	5.48×10^{-5}	1.42×10^{-5}
(*12*)	375	1.10×10^{-4}	3.07×10^{-5}
	400	2.49×10^{-4}	5.50×10^{-5}
o-Xylene	290	8.66×10^{-6}	2.88×10^{-4}
(present	300	1.26×10^{-5}	4.39×10^{-4}
study)	310	1.91×10^{-5}	6.74×10^{-4}

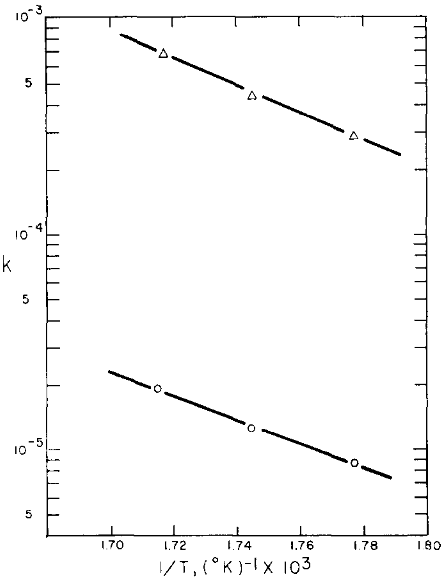

FIG. 3. Arrhenius plot of rate constants (k_a and k_r) from present study. △, k_r; ○, k_a.

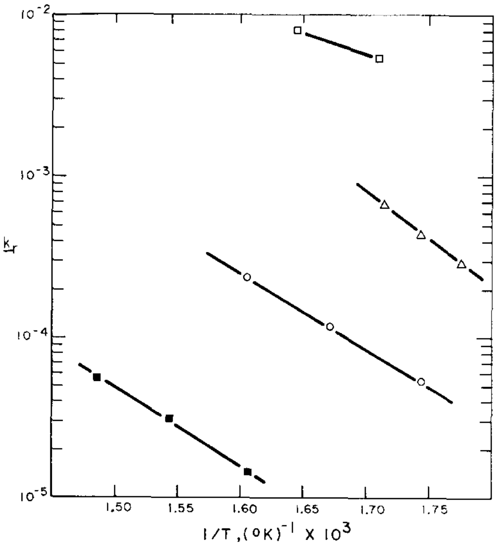

FIG. 4. Arrhenius plots of k_r from naphthalene (*3*), toluene (*9*), benzene (*12*), and *o*-xylene (present study). □, naphthalene; ○, toluene; ■, benzene; △, *o*-xylene.

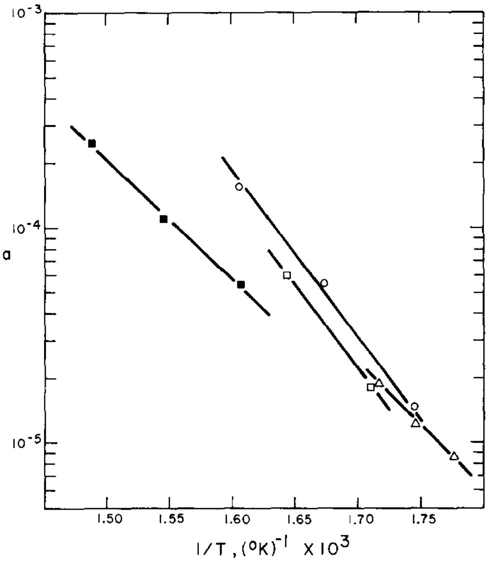

FIG. 5. Arrhenius plots of k_a from naphthalene (*3*), toluene (*9*), benzene (*12*), and *o*-xylene (present study). □, naphthalene; ○, toluene; ■, benzene; △, *o*-xylene.

It should be noted that the relationships were used with the rate equations to produce the solid lines shown in Figs. 1 and 2. This produces a general correlation which is satisfactory. Note that the general correlation line will not fit an individual set of data quite as well as the line based on that set alone.

Table 4 shows the rate constants obtained for Model 1 for toluene (*9*), naphthalene (*3*), benzene (*12*), and *o*-xylene oxidation on the same catalyst. These values are plotted in Figs. 4 and 5 as Arrhenius plots. The k_r values for different hydrocarbons have a 1000-fold range. The agreement in k_a values as shown in Fig. 5 supports criterion 3, showing that the specific rate of oxygen adsorption onto the catalyst surface is independent of the hydrocarbon being oxidized.

A second order dependence of benzene reaction rate on oxygen at low concentration has been reported by Ioffe and Lyubarskii (*15*). This order dependence would be evidence against the steady-state model as presented. The work of Ioffe and Lyubarskii, however, appears to have an internal inconsistency. Figure 7 (Ref. *15*) shows that the rate dependence on oxygen concentration is second order. However, the data from Fig. 8 (Ref. *15*) show an approximately first order dependence. In the present study on *o*-xylene, reaction rates were determined at low oxygen concentrations, certainly within the range at which Ioffe and Lyubarskii found a second order rate dependence, although the comparison for different catalysts may not be valid. However, there is no evidence of a second order rate dependence in this region in the present work on *o*-xylene.

CONCLUSIONS

Various kinetic models have been tested on data for *o*-xylene, benzene, and toluene oxidation on the same vanadium oxide catalyst. The steady-state model provided the best description of the data. Values of k_a obtained for *o*-xylene in the present work agree favorably with those obtained previously for naphthalene, toluene, and benzene oxidation on the same catalyst, thus providing further support for the model. In addition, reaction rates were obtained at low oxygen concentrations and showed no tendency to a second order rate dependence.

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REFERENCES

1. CALDERBANK, P. H., *Ind. Chem.*, 291 (1952).
2. MARS, P., AND VAN KREVELEN, D. W., *Chem. Eng. Sci. (Special Suppl.)* **3**, 41 (1954).
3. SHELSTAD, K. A., DOWNIE, J., AND GRAYDON, W. F., *Can. J. Chem. Eng.* **38**, 102 (1960).
4. SIMARD, G. L., STEGER, J. F., ARNOTT, R. J., AND SIEGEL, L. A., *Ind. Eng. Chem.* **47**, 1924 (1955).
5. VRBASKI, T., *J. Phys. Chem.* **69**, 3092 (1965).
6. BHATTACHARYYA, S. K., JANAKIRAM, K., AND GANGULY, N. D., *J. Catal.* **8**, 128 (1967).
7. HERTEN, J., AND FROMENT, G. F., *Ind. Eng. Chem. Process Des. Develop.* **7**, 516 (1968).

8. Vrbaski, T., and Mathews, W. K., *J. Phys. Chem.* **69,** 457 (1965).

9. Downie, J., Shelstad, K. A., and Graydon, W. F., *Can. J. Chem. Eng.* **39,** 201 (1961).

10. Hayashi, R., Hudgins, R. R., and Graydon, W. F., *Can. J. Chem. Eng.* **41,** 220 (1963).

11. Mann, R. F., and Downie, J., *Can. J. Chem. Eng.* **46,** 71 (1969).

12. Jaswal, I. T., Mann, R. F., Juusola, J. A., and Downie, J., *Can. J. Chem. Eng.* **47,** 284 (1969).

13. Loftus, J., and Satterfield, C. N., *J. Phys. Chem.* **69,** 909 (1965).

14. Miss Nga Chu, Private communication (1968).

15. Ioffe, I. I., and Lyubarskii, A. G., *Kinet. Catal. (USSR)* **3,** 223 (1962).