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The Kinetics of the Vapor-Phase Ammoxidation of *m*-Xylene over a Vanadium Catalyst

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The kinetics of the vapor-phase ammoxidation of *m*-xylene and *m*-tolunitrile over a vanadium oxide catalyst were studied in a flow system. The reaction rate data obtained were correlated by the rate equation based upon the Langmuir-Hinshelwood mechanism, where the adsorption of *m*-xylene was strong. From the result of the experiments it was suggested that the reaction scheme consisted of four parallel routes: (1) the step-by-step ammoxidation of *m*-xylene to isophthalonitrile *via* *m*-tolunitrile; (2) the direct ammoxidation to isophthalonitrile from *m*-xylene; (3) the formation of carbon oxides and hydrogen cyanide *via* *m*-tolunitrile and (4) the direct formation of carbon oxides and hydrogen cyanide from *m*-xylene. The activation energies for the reaction of *m*-xylene and *m*-tolunitrile were 43.7 and 31.2 kcal/mol respectively in the range from 396 to 420°C.

Recently the vapor-phase ammoxidation of xylenes has had considerable importance as a commercial method for producing dicyanobenzenes. The great majority of studies in this field have dealt with the determination of the conditions for producing dicyanobenzenes.[1,2] Several kinetic studies have now been made, especially with regard to the catalytic ammoxidation of toluene over vanadium-oxide catalysts.[3,4] However, few data on the reaction kinetics of the catalytic ammoxidation of xylenes to dicyanobenzenes have been presented.[1,5]

The present study is an attempt to clarify the reaction kinetics and mechanism of the ammoxidation of *m*-xylene over a vanadium-oxide catalyst.

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[1] D. J. Hadley, *Chem. & Ind.*, **1961**, 238.

[2] Y. Ogata and K. Sakanishi, *Kagaku-Kojo*, **8**, No. 4, 70 (1964).

[3] H. Tanabe, F. Araki and H. Kobayashi, The 5th Symposium on the Reaction Engineering of Japan, Tokyo, Oct., 1965.

[4] Y. Ogata, Y. Sawaki and K. Sakanishi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 1542 (1964).

[5] Y. Ogata and K. Sakanishi, The 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966; *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 2294 (1966).

Experimental

Experimental Apparatus and Procedures. The reaction was carried out in a fixed-bed reaction system, the flow diagram for which is seen in Fig. 1. The reactor consisted of a 10 mm i. d. stainless steel tube containing a central thermowell (3 mm o.d.). The reactor was loaded with 2 or 4 cc of a catalyst and immersed in an electrically heated and stirred salt bath. The temperature gradients in the catalyst bed were small in all the reaction runs; their maximum was 2°C. *m*-Xylene was added by mans of the quantitative injector, to a vaporizer which had been heated at 130°C.

A gas mixture containing known amounts of oxygen, nitrogen, ammonia, and *m*-xylene was passed through the reactor for 2 hr under the desired experimental conditions prior to the main run. After this period, a steady-state condition in the system was obtained. The quantitative collection of the products was then started by connecting the product-collecting section to the system. At the end of a day's operation, nitrogen was passed through the reactor for about 30 min.

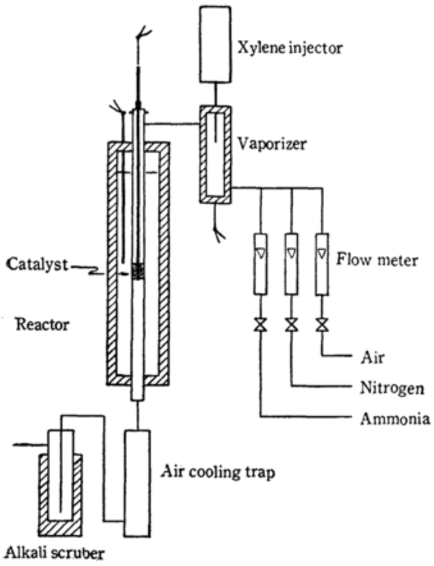

Fig. 1. Flow diagram of apparatus.

Analytical Procedure. Isophthalonitrile and *m*-tolunitrile in a methanol solution, in which the reaction products in a trap were dissolved, were determined by ultraviolet absorption spectroscopy. *m*-Cyanobenzoic acid and an unidentified tarry matter were found in the methanol solution, but they were negligible during most runs.

Unreacted *m*-xylene, carbon dioxide, and carbon oxide in the effluent gas from the reactor were determined by gas chromatography. A molecular sieve 13 X column was used for carbon oxide, a silica gel column for carbon dioxide, and a column of 30 wt% dioctylphthalate on Chromsorb W for *m*-xylene. In most runs only a trace of carbon oxide was found in the effluent gas.

The amounts of hydrogen cyanide and carbon dioxide absorbed in the alkali scrubber were determined by titration.

Materials. *m*-Xylene was obtained from Chevron Chem., Inc. It was proved 98.7% pure by gas-liquid chromatographic analysis. *m*-Tolunitrile was obtained from the Tokyo Kasei Co. It was purified by distillation. Bp 113°C/41 mmHg.

Ammonia and nitrogen were taken from cylinders containing the compressed gas. They were dried over calcium oxide before use. Air was taken from the air compressor. It was passed through a silica gel column before use.

Catalyst Preparation. Alundum carriers (27 g) sieved between 0.5 to 1.0 mm were impregnated with a solution prepared from 3.0 g of vanadium pentoxide, 10.4 g of oxalic acid and 20 cc of water. The impregnated carriers were dried at 70°C and calcinated in air at 550°C for 4 hr, after which the calcinated catalyst was aged under catalytic conditions for 2 days before use. This catalyst had a surface area of 0.5 m²/g after the reaction.

Results and Treatment of Data

The results of the catalytic ammoxidation of *m*-xylene are shown in Tables 1 to 4. In order to

TABLE 1. RATE DATA FOR THE AMMOXIDATION OF *m*-XYLENE AT 420°C

Concentration of *m*-xylene 0.88−2.57%
Ratio of ammonia to *m*-xylene 5
Concentration of air Residue

Feed rate of *m*-xylene mmol/hr	Space velocity hr⁻¹	P_{XO} atm	Conversion of *m*-xylene	Conversion to		
				IPN[*2]	*m*-TN[*3]	CO_2, HCN
3.00	2210	0.015	0.850	0.287	0.375	0.188
5.08	3790	0.015	0.500	0.146	0.252	0.102
6.03	4500	0.015	0.380	0.112	0.185	0.083
8.08	6000	0.015	0.238	0.067	0.105	0.066
5.08[*1]	1900	0.015	0.914	0.393	0.313	0.208
6.03[*1]	2250	0.015	0.859	0.297	0.388	0.174
3.00	3790	0.0088	0.870	0.330	0.330	0.210
5.08	2210	0.0257	0.501	0.143	0.273	0.085

[*1] Catalyst volume is 4 cc (4.53 g). Others are 2 cc (2.36 g).
[*2] Isophthalonitrile [*3] *m*-Tolunitrile

TABLE 2. EFFECT OF AMMONIA CONCENTRATION AT 420°C

Catalyst volume 2 cc
Space velocity 3790 hr^{-1}
Initial partial pressure of *m*-xylene 0.015 atm
Feed rate of *m*-xylene 5.08 mmol/hr

Mole ratio of ammonia to *m*-xylene	Conversion of *m*-xylene	Conversion to		
		IPN	*m*-TN	CO_2, HCN
3	0.537	0.171	0.249	0.117
5	0.500	0.146	0.252	0.102
7	0.547	0.163	0.269	0.116

TABLE 3. EFFECT OF OXYGEN CONCENTRATION AT 420°C

Catalyst volume 2 cc
Space velocity 2210 hr^{-1}
Initial partial pressure of *m*-xylene 0.015 atm
Initial partial pressure of ammonia 0.075 atm
Feed rate of *m*-xylene 3.00 mmol/hr

Initial partial pressure of *m*-xylene, atm	Conversion of *m*-xylene	Conversion to		
		IPN	*m*-TN	CO_2, HCN
0.191	0.850	0.287	0.375	0.188
0.168	0.862	0.289	0.377	0.196
0.147	0.863	0.314	0.370	0.179
0.126	0.783	0.272	0.361	0.150

TABLE 4. EFFECT OF REACTION TEMPERATURE

Catalyst volume 2 cc
Space velocity 2210 hr^{-1}
Initial partial pressure of *m*-xylene 0.015 atom
Ratio of ammonia to *m*-xylene 5

Reaction temp. °C	Conversion of *m*-xylene	Conversion to		
		IPN	*m*-TN	CO_2, HCN
420	0.850	0.287	0.375	0.188
416	0.725	0.205	0.385	0.135
406	0.402	0.113	0.227	0.062
396	0.244	0.069	0.134	0.041

know the extent to which the homogeneous gas-phase reactions and also the reactions on the reactor wall participate in the catalytic reaction, non-catalytic runs were carried out under conditions similar to those of catalytic runs. More than ninety-eight mole per cent of *m*-xylene was recovered unchanged. Therefore, no correction in the measured catalytic rates was made. Also, in order to ascertain the mass-transfer effect on the rate, a few experiments were carried out at a faster gas flow rate but otherwise under unchanged conditions. Since identical results were obtained, it was concluded that the mass-transfer effect was not significant.

The zero-order plot of *m*-xylene disappearance at 420°C is shown in Fig. 2. The linear relationship held to about seventy-five per cent reaction, indicating that the rate of the reaction of *m*-xylene is nearly independent of the concentration of *m*-xylene under the given conditions.

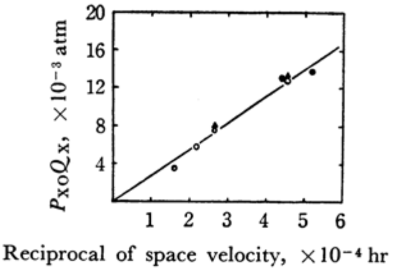

Fig. 2. Zero order plot of *m*-xylene disappearance at various initial concentration of *m*-xylene at 420°C.

P_{XO}: ○, 0.015 atm; ●, 0.015 atm (catalyst volume 4 cc); △, 0.008 atm; ▲, 0.0275 atm

In Figs. 3 and 4 data on the formation of individual products and on the conversion of *m*-xylene are plotted as a function of the initial concentration of ammonia or oxygen in the reaction mixture. These data indicate that the rate

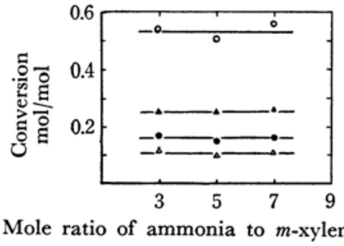

Fig. 3. Effect of ammonia concentration at 420°C.

Initial concentration of *m*-xylene 1.5%
○, Conversion of *m*-xylene; ▲, Conversion to *m*-tolunitrile; ●, Conversion to isophthalonitrile; △, Conversion to carbon oxides and hydrogen cyanide

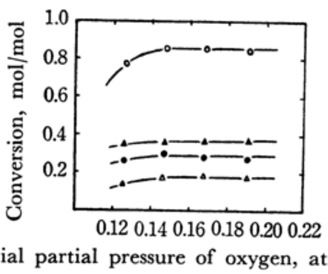

Fig. 4. Effect of oxygen concentration at 420°C.

Initial concentration of *m*-xylene 1.5%
Initial concentration of ammonia 7.5%
○, Conversion of *m*-xylene; ▲, Conversion to *m*-tolunitrile; ●, Conversion to isophthalonitrile; △, Conversion to carbon oxides and hydrogen cyanide

Table 5. Rate data for ammoxidation of *m*-tolunitrile at 420°C

Catalyst volume	2 cc
Concentration of *m*-tolunitrile	0.6−1.2%
Ratio of ammonia to *m*-tolunitrile	5

Feed rate of *m*-tolunitrile mmol/hr	Space velocity hr^{-1}	P_{MO} atm	Conversion of *m*-tolunitrile	Conversion to		
				IPN	CO_2	HCN
3.2	2990	0.012	0.769	0.705	0.047	0.017
3.2	2990	0.012	0.758	0.693	0.050	0.015
5.27	4920	0.012	0.589	0.540	0.039	0.010
5.27	4920	0.012	0.594	0.543	0.041	0.010
3.2	3580	0.010	0.749	0.678	0.057	0.014
5.27	5900	0.010	0.603	0.557	0.035	0.011
5.27	5900	0.010	0.577	0.537	0.030	0.010
3.2	4480	0.008	0.729	0.655	0.059	0.015
3.2	4960	0.006	0.625	0.560	0.050	0.015

of the reaction of *m*-xylene and the rate of the formation of individual products are not influenced by either the ammonia or oxygen concentration throughout the reaction under the conditions given in Table 1.

In Fig. 5 data on the formation of individual products are plotted as a function of the reciprocal of the gas velocity, which is directly proportional to the contact time. The data in Fig. 5 indicate that there are two routes for the formation of isophthalonitrile: (1) isophthalonitrile is formed by a process parallel to the formation of *m*-tolunitrile and other products, and (2) isophthalonitrile is formed by a consecutive route in which *m*-tolunitrile is an intermediate. At a low conversion of *m*-xylene, isophthalonitrile seemed to be predominantly formed from *m*-xylene directly by way of the parallel reaction. The rate of the formation of isophthalonitrile also increased remarkably when the conversion of *m*-xylene was high. This suggests that the rate of the reaction of *m*-tolunitrile is inhibited by *m*-xylene.

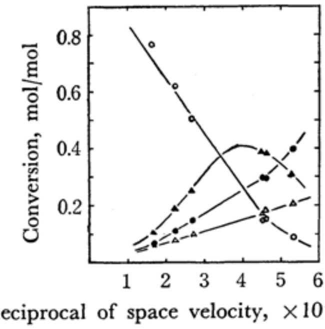

Fig. 5. Effect of contact time at 420°C.
Initial concentration of *m*-xylene 1.5%
Initial concentration of ammonia 7.5%
○, Unconverted *m*-xylene; ▲, Conversion to *m*-tolunitrile; ●, Conversion to isophthalonitrile; △, Conversion to carbon oxides and hydrogen cyanide

Since *m*-tolunitrile was the main intermediate in the consecutive route leading to isophthalonitrile, as has been described above, the catalytic ammoxidation of *m*-tolunitrile was carried out (Tables 5 and 6).

Table 6. Effect of reaction temperature for ammoxidation of *m*-tolunitrile

Catalyst volume	2 cc
Space velocity	4480 hr^{-1}
Concentration of *m*-tolunitrile	0.8%
Ratio of ammonia to *m*-tolunitrile	5

Reaction temp. °C	Conversion of *m*-tolunitrile	Conversion to		
		IPN	CO_2	HCN
420	0.729	0.655	0.059	0.015
410	0.590	0.528	0.050	0.012
400	0.475	0.417	0.047	0.011

In Fig. 6 the first-order plot of *m*-tolunitrile disappearance at 420°C at four different initial concentrations of *m*-tolunitrile is shown. The

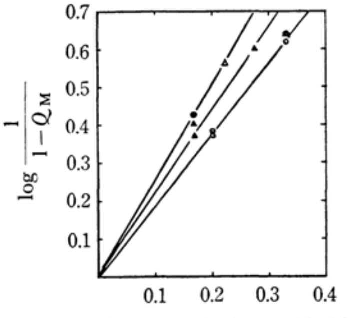

Fig. 6. First order plot of *m*-tolunitrile disappearance at various initial concentration of *m*-tolunitrile at 420°C.

P_{XO}: ○, 0.012 atm; ▲, 0.01 atm;
△, 0.008 atm; ●, 0.006 atm

results indicate that the reaction of *m*-tolunitrile is apparently a first-order reaction at low *m*-tolunitrile concentrations (less than 0.008 atm). At higher concentrations, however, the slope of the line in a plot tends to become moderate.

Under given conditions it was assumed that the flow of the gas stream was piston-like and that the degradation reaction of isophthalonitrile was negligible, because isophathlonitrile is stable,⁶⁾ especially in the presence of unreacted xylene. Since air was used in excess, the volume change of the gas in the reaction was ignored.

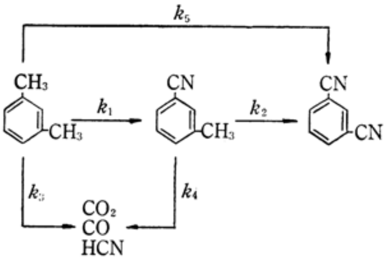

Fig. 7. Reaction scheme for ammoxidation of *m*-xylene.

In view of the above facts, the following rate expressions for the reaction scheme (Fig. 7) were chosen:

$$r_X = -dC_X/d(V/F) = k_X \tag{1}$$

$$r_M = dC_M/d(V/F) = k_1 - k_X P_M/P_X \tag{2}$$

$$r_D = dC_D/d(V/F) = k_5 + k_2 P_M/P_X \tag{3}$$

$$r_B = dC_B/d(V/F) = k_3 + k_4 P_M/P_X \tag{4}$$

Equations (1) to (4) were recast into Eqs. (10) to (13) by substituting Eqs. (5) to (9):

$$P_X = P_{XO}(1-Q_X) \tag{5}$$

$$P_X = C_X R T_O \tag{6}$$

$$P_M = P_{XO} Q_M = C_M R T_O \tag{7}$$

$$P_D = P_{XO} Q_D = C_D R T_O \tag{8}$$

$$P_B = P_{XO} Q_B = C_B R T_O \tag{9}$$

$$dQ_X/d(V/F) = k_X R T_O/P_{XO} \tag{10}$$

$$dQ_M/d(V/F) = k_1 R T_O/P_{XO} - k_M R T_O Q_M/P_{XO}(1 - Q_X) \tag{11}$$

$$dQ_D/d(V/F) = k_5 R T_O/P_{XO} + k_2 R T_O Q_M/P_{XO}(1 - Q_X) \tag{12}$$

$$dQ_B/d(V/F) = k_3 R T_O/P_{XO} + k_4 R T_O Q_M/P_{XO}(1 - Q_X) \tag{13}$$

Integrating Eqs. (10) to (13), they lead to Eqs. (14) to (17):

$$P_{XO} Q_X = k_X R T_O (V/F) \tag{14}$$

$$Q_M = \frac{\mathrm{s}}{1-\mathrm{R}}\{1-Q_X)^{\mathrm{R}} - (1 - Q_X)\} \tag{15}$$

$$Q_D/Q_X = \frac{k_5}{k_X} + \frac{k_2 \mathrm{s}}{k_X(1-\mathrm{R})} \times \left[\frac{1}{\mathrm{R}}\{1-(1-Q_X)^{\mathrm{R}}\} - Q_X\right]\frac{1}{Q_X} \tag{16}$$

$$Q_B/Q_X = \frac{k_3}{k_X} + \frac{k_4 \mathrm{s}}{k_X(1-\mathrm{R})} \times \left[\frac{1}{\mathrm{R}}\{1-(1-Q_X)^{\mathrm{R}}\} - Q_X\right]\frac{1}{Q_X} \tag{17}$$

Using the data in Table 1, the linear relationship for Eq. (14) held to a high conversion of *m*-xylene as has been shown in Fig. 2.

For Eq. (15) a relatively good linear relationship was obtained, as is shown in Fig. 8, where R was one-fourth.

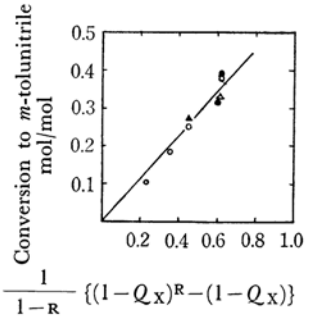

Fig. 8. Relationship between Q_M and Q_X. R is one-fourth

As is shown in Fig. 9, a linear relationship was obtained for Eqs. (16) and (17), too.

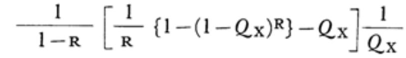

Fig. 9. Relationship between Q_D (or Q_B) and Q_X.
R is one-fourth

Broken line: Ratio of Q_D to Q_X
Solid line: Ratio of Q_B to Q_X

TABLE 7. RATE CONSTANTS FOR AMMOXIDATION OF *m*-XYLENE AT 420°C

$k_X R T_O$ atm/hr	k_X/k_M	k_1/k_X	k_3/k_X	k_5/k_X	k_2/k_M	k_4/k_M
27.2	4	0.55	0.20	0.25	0.81	0.19

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6) S. Saito and N. Ohta, *Yuki Gosei Kagaku Kyokaishi (J. Soc. Org. Syn. Chem. Japan)*, **22**, 730 (1964).

TABLE 8. RATE DATA FOR AMMOXIDATION OF m-TOLUNITRILE IN THE PRESENCE OF m-XYLENE AT 420°C*2

Feed rate mmol/hr		Initial partial pressure, atm		Effluent rates of products, mmol/hr							
				Unreacted xylene		IPN		m-TN		CO_2, HCN*1	
m-TN	m-Xylene	m-TN	m-Xylene	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
3.2		0.008				2.04		0.85		0.23	
3.2	2.91	0.008	0.0073	0.77	0.66	1.31	1.63	3.47	3.29	0.41	0.54

*1 Calculated as m-xylene and m-tolunitrile converted to carbon oxides and hydrogen cyanide.

*2 Space velocity 4480 hr^{-1}; Catalyst volume 2 cc

The values of k_X, k_M, k_1, k_2, k_3, k_4, and k_5 were found from the slopes and interecepts in Figs. 2, 8, and 9. They are listed in Table 7. The sum of either the ratio of k_1, k_3, and k_5 to k_X or the ratio of k_2 and k_4 to k_M has been found to be unity.

Moreover, in order to establish that the above-mentioned kinetic model for the reaction scheme is reasonable, the ammoxidation of m-tolunitrile was carried out in the presence of m-xylene. The close agreement between the observed and calculated flow rates of individual products is illustrated in Table 8. This result indicates that the proposed reaction scheme and stoichiometries are consistent with all the experimental observations.

Figure 10 shows the Arrhenius plot of the over-all conversion of m-xylene, since the over-all conversion of m-xylene is directly proportional to the specific rate constant at a constant initial concentration of m-xylene for a fixed amount of catalyst. The activation energy for the over-all reaction of m-xylene in the temperature range studied was 43.7 kcal/mol.

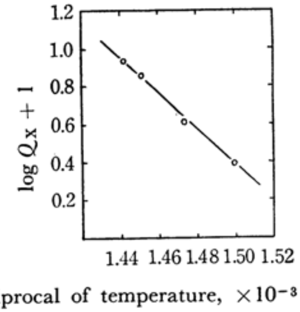

Fig. 10. Arrhenius plot of the over all conversion of m-xylene from 396 to 420°C.

The following rate expression for the ammoxidation of m-tolunitrile was chosen in order to correlate the data in Table 5 and Fig. 6:

$$r_M = -dC_M/d(V/F) = k_M'K_MP_M/(1+K_MP_M) \tag{18}$$

$$P_M = P_{MO}(1-Q_M) \tag{19}$$

From Eqs. (7), (18), and (19), the rate of the reaction of m-tolunitrile may be written:

$$dQ_M/d(V/F) = \frac{k_M'RT_OK_M(1-Q_M)}{1+K_MP_{MO}(1-Q_M)} \tag{20}$$

Integrating Eq. (20) leads to Eq. (21):

$$\frac{1}{P_{MO}Q_M}\ln\frac{1}{1-Q_M} = \frac{k_M'RT_OK_M\,V}{P_{MO}Q_M\,F} - K_M \tag{21}$$

Eq. (21) was used to test the effectiveness of this treatment in the correlation of the experimental results. The straight-line relationship was a relatively good fit of the data, as is shown in Fig. 11. The values of K_M and $k_M'RT_O$ were 7.5×10 atm^{-1} and 9.7×10 atm/hr respectively, calculating from the slope and intercept of the line in Fig. 11.

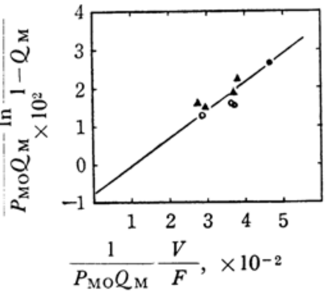

Fig. 11. Relationship between P_{MO} and Q_M.

The rate of the reaction of m-tolunitrile was also found to be the first-order for concentrations of m-tolunitrile below 0.008 atm. Thus, the rate of

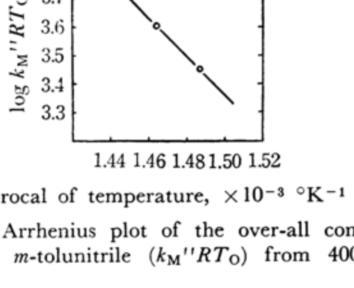

Fig. 12. Arrhenius plot of the over-all conversion of m-tolunitrile ($k_M''RT_O$) from 400 to 420°C.

the reaction of *m*-tolunitrile can be represented by Eq. (22) under the conditions given in Table 6:

$$r_{\rm M} = -{\rm d}C_{\rm M}/{\rm d}(V/F) = k_{\rm M}''P_{\rm M} \qquad (22)$$

The Arrhenius plot of the specific rate constants, which were calculated in a manner similar to that used for *m*-xylene, is shown in Fig. 12. The activation energy for the over-all reaction of *m*-tolunitrile in the temperature range studied was 31.2 kcal/mol.

Discussion

The results described above suggest that the rate-controlling step in this reaction is the chemical reaction on the catalyst surface, while the rates of the adsorption of the reactants and of the desorption of the products are rapid. The rate data also suggest that the reaction of *m*-tolunitrile is affected by the adsorption of *m*-xylene on the catalyst surface.

In interpreting the proposed reaction kinetics based upon the experimental data, a treatment based upon the Langmuir-Hinshelwood mechanism, in which the rate-controlling step in the reaction is the chemical reaction on the catalyst surface, is used. In view of the experimental findings that the rate of the reaction is independent of the concentrations of ammonia and oxygen under the given conditions, it is assumed that the surface concentrations of the adsorbed ammonia and oxygen are constant, or that they do not control the reaction rates under the given conditions. The over-all reaction rate of *m*-xylene can, therefore, be represented by the following relationship:

$$r_{\rm X} = \frac{k_{\rm X}K_{\rm X}P_{\rm X}}{1 + K_{\rm M}P_{\rm M} + K_{\rm X}P_{\rm X} + \sum K_iP_i} \qquad (23)$$

in which K_i and P_i are the adsorption equilibrium constant and the partial pressure of other compounds, such as isophthalonitrile and carbon oxides.

In Eq. (23), if the adsorption of *m*-xylene is strong, that is, if $1+K_{\rm M}P_{\rm M}+\sum K_iP_i \ll K_{\rm X}P_{\rm X}$, Eq. (23) becomes:

$$r_{\rm X} = k_{\rm X}'K_{\rm X}P_{\rm X}/K_{\rm X}P_{\rm X} = k_{\rm X} \qquad (24)$$

which is consistent with Eq. (1).

In the same manner, the over-all reaction rate of *m*-tolunitrile in the presence of *m*-xylene can be written by Eq. (25):

$$r_{\rm M} = \frac{k_{\rm M}'K_{\rm M}P_{\rm M}}{1 + K_{\rm M}P_{\rm M} + K_{\rm X}P_{\rm X} + \sum K_{\rm i}P_{\rm i}} \qquad (25)$$

If $1+K_{\rm M}P_{\rm M}+\sum K_{\rm i}P_{\rm i}$ is negligible for $K_{\rm X}P_{\rm X}$, it becomes:

$$r_{\rm M} = k_{\rm M}'K_{\rm M}P_{\rm M}/K_{\rm X}P_{\rm X} = k_{\rm M}P_{\rm M}/P_{\rm X} \qquad (26)$$

which is consistent with the second term in Eq. (2).

That $k_{\rm M}$ is one-fourth of $k_{\rm X}$, though $k_{\rm M}'$ is about 3.5 times the size of $k_{\rm X}$, is probably, in view of Eq. (26), ascribed to the strong adsorption of *m*-xylene on the catalyst surface. The adsorption equilibrium constant of *m*-xylene is, therefore, 1.1×10^3 atm^{-1}, which is about fourteen times the size of $K_{\rm M}$. This indicates that the relationship of Eqs. (1) to (4) is adaptable in the concentration range of *m*-xylene of more than 0.002 atm.

From the fact that these results are in good agreement with the experimental data, the treatment based upon the Langmuir-Hinshelwood mechanism appears to provide a good characterization of the kinetics of the ammoxidation of *m*-xylene.

The rate of the reaction of *m*-tolunitrile, Eq. (18), can be represented by a similar treatment based upon the Langmuir-Hinshelwood mechanism. It can also be represented by Eq. (22), where $1+K_{\rm M}P_{\rm M}$ is nearly unity. The rate data indicate that the relationship for Eq. (22) is adaptable in the concentration range of *m*-tolunitrile of less than 0.008 atm.

The apparent activation energy for the reaction of *m*-xylene was 43.7 kcal/mol, which is compar able to that reported by Hadley[1] (40 kcal/mol for *p*-xylene over a vanadium-oxide catalyst supported on alumina). On the other hand, the apparent activation energy for the reaction of *m*-tolunitrile was 31.2 kcal/mol, which is considerably smaller than that for *m*-xylene. This difference appears to be ascribable to the heat of the adsorption of *m*-tolunitrile, since the specific rate constant of *m*-tolunitrile, $k_{\rm M}''$, involves the adsorption equilibrium constant for *m*-tolunitrile, as Eqs. (18) and (22) show.

From the results on the treatment of data, it was found that *m*-xylene was reacted by a parallel consecutive mechanism, one which was similar to an oxidation mechanism proposed by Clark[7] and Novella[8] for *o*-xylene or by Vrbaski for *o*-methylbenzylalcohol[9] and *o*-tolualdehyde[10]. The reaction kinetics for the catalytic oxidation of *o*-xylene studied by Clark[7] is also similar to that of this study. It may, therefore, be suggested that the reaction process taking place on the catalyst surface is similar for both reactions.

The presence of a path which forms isophthalonitrile directly from *m*-xylene suggests that the adsorption of *m*-xylene takes place by way of both methyl groups. A similar suggestion has been reported by Rafikov[11] and Ogata[5].

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The relationship between the selectivities for each product and the reaction kinetics is of interest for a better understanding of the reaction processes which take place on the catalyst surface. This matter will be discussed in later papers.

Nomenclature

C_X	Concentration of *m*-xylene, mol cc^{-1}
C_M	Concentration of *m*-tolunitrile, mol cc^{-1}
C_D	Concentration of isophthalonitrile, mol·cc^{-1}
C_B	Concentrations of carbon oxides and hydrogen cyanide, as the basis of *m*-xylene, mol cc^{-1}
k_X	Specific rate constant of the reaction of *m*-xylene, mol cc^{-1} hr^{-1}
k_M	Specific rate constant of the reaction of *m*-tolunitrile in the presence of *m*-xylene, mol cc^{-1} hr^{-1}
k_M'	Specific rate constant of the reaction of *m*-tolunitrile in the absence of *m*-xylene, mol cc^{-1} hr^{-1}
k_M''	Specific rate constant of the reaction of *m*-tolunitrile for the first-order reaction, hr^{-1}
k_1	Specific rate constant of formation of *m*-tolunitrile from *m*-xylene, mol cc^{-1} hr^{-1}
k_2	Specific rate constant of formation of isophthalonitrile from *m*-tolunitrile, mol·cc^{-1} hr^{-1}
k_3	Specific rate constant of direct formation of carbon oxides and hydrogen cyanide from *m*-xylene, mol cc^{-1} hr^{-1}
k_4	Specific rate constant of formation of carbon oxides and hydrogen cyanide from *m*-tolunitrile, mol cc^{-1} hr^{-1}
k_5	Specific rate constant of direct formation of isophthalonitrile from *m*-xylene, mol·cc^{-1} hr^{-1}
K_X	Adsorption equilibrium constant of *m*-xylene, atm^{-1}
K_M	Adsorption equilibrium constant of *m*-tolunitrile, atm^{-1}
P_X	Partial pressure of *m*-xylene, atm
P_{XO}	Intial partial pressure of *m*-xylene, atm
P_M	Partial pressure of *m*-tolunitrile, atm
P_{MO}	Initial partial pressure of *m*-tolunitrile, atm
P_D	Partial pressure of isophthalonitrile, atm
P_B	Partial pressure of carbon oxides and hydrogen cyanide, atm
Q_X	Conversion of *m*-xylene, mol mol^{-1}
Q_M	Conversion of or to *m*-tolunitrile, mol·mol^{-1}
Q_D	Conversion to isophthalonitrile, mol mol^{-1}
Q_B	Conversion to carbon oxides and hydrogen cyanide, mol mol^{-1}
r_X	Rate of reaction of *m*-xylene, mol cc^{-1}·hr^{-1}
r_M	Rate of reaction of or rate of formation of *m*-tolunitrile, mol cc^{-1} hr^{-1}
r_D	Rate of formation of isophthalonitrile, mol cc^{-1} hr^{-1}
r_B	Rate of formation of carbon oxides and hydrogen cyanide, mol cc^{-1} hr^{-1}
R	Ratio of k_M to k_X
S	Ratio of k_1 to k_X
V	Volume of catalyst, cc
F	Flow rate of gas (NTP), cc hr^{-1}

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