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KINETICS OF THE CATALYTIC VAPOR-PHASE AMMOXIDATION OF TOLUENE OVER CHROMIUM OXIDE*

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Abstract—The kinetics of the catlytic vapor-phase ammoxidation of toluene over a chromium oxide catalyst have been studied in a flow system at atmospheric pressure. The reaction consists of the oxidation of toluene and the ammoxidation of formed benzaldehyde. The rate of ammoxidation of toluene is expressed as $k[\mathrm{PhCH_3}]^{0\cdot45}\,[\mathrm{O_2}]^{0\cdot45}$ and independent of concentrations of ammonia and products. The rate of ammoxidation of benzaldehyde is equal to that of ammonolysis of benzaldehyde, and is expressed as $k[\mathrm{PhCHO}]^{0\cdot47-0\cdot53}\,[\mathrm{NH_3}]^{0\cdot42-0\cdot44}$, which is independent of oxygen and products, but the formation of benzonitrile is dependent on oxygen. The apparent activation energies for ammoxidations of toluene and benzaldehyde are ca. 23 and ca. 11 kcal/mole, respectively. These results suggest a main pathway involving benzaldehyde and benzylidenimine for the ammoxidation. The rate equations are interpreted in terms of the Langmuir–Hinshelwood mechanism.

The catalysts developed for the catalytic vapor-phase ammoxidation of aromatic hydrocarbons, usually contain vanadium pentoxide as the main component,[1] and others are tungstate[2] and molybdenum trioxide.[3] We have discovered that chromium oxide (Cr_2O_3) is an excellent catalyst for the ammoxidation of toluene. The selectivity of benzonitrile over chromium oxide is superior to vanadium oxide, the optimum yield being over 80%.[4] Several kinetic studies of ammoxidation of aromatic hydrocarbons, e.g. toluene[5–7] and xylenes[8–10], used V_2O_5 catalysts. The present study was undertaken to elucidate the mechanistic feature of the ammoxidation of toluene over chromium oxide in terms of the kinetics for the reactions of toluene and intermediary benzaldehyde, and the effects of additives.

RESULTS AND DISCUSSION†

Examination of mass-transfer effect for ammoxidation of toluene. The effect of mass-transfer on the rate of ammoxidation of toluene was examined at a fixed gas space velocity (3600 hr^{-1}). Both toluene conversion and benzonitrile yield were almost constant (32–38%) at 400° with catalyst volume of 2·5–8·0 ml. Hence, the rate is not determined by diffusion but by reaction on catalyst surface.

Comparison of reactivity. Table 1 shows the reactivity of toluene for ammoxidation, oxidation and ammonolysis, which are in the order:

$$\text{ammoxidation} > \text{oxidation} > \text{ammonolysis}$$

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* Contribution No. 111.

† For the nomenclature of symbol letters, see the last section.

Oxidation of toluene may give benzaldehyde, while ammonolysis of toluene may give benzylamine as the primary intermediate. The ammonolysis is so slow that it cannot be the main pathway. Since oxidation of toluene yields benzaldehyde, this seems to be a primary intermediate in the ammoxidation. Table 2 shows that the order of reactivities of benzaldehyde is as follows:

$$\text{ammoxidation} \simeq \text{ammonolysis} \gg \text{oxidation}$$

Oxidation of benzaldehyde cannot be involved in the main pathway for benzonitrile formation, since the rate of oxidation of benzaldehyde is slower than that of ammoxidation.* Therefore, ammoxidation of toluene goes mainly by way of benzaldehyde.

TABLE 1. REACTIVITIES OF TOLUENE AT 403° WITH CATALYST VOLUME OF 5·0 ml AND GAS SPACE VELOCITY OF 3600 hr^{-1}

Reaction	Conversion of toluene (mole %)	Yield of benzonitrile (mole %)	Yield of benzaldehyde (mole %)
Ammoxidation[a]	25·9	23·6	0
Oxidation[b]	14·2	—	5·7
Ammonolysis[c]	4·4	2·8	—

[a] p_{TO} 1·33 × 10^{-2} atm, p_O 13·3 × 10^{-2} atm, p_A 6·7 × 10^{-2} atm.
[b] p_{TO} 1·33 × 10^{-2} atm, p_O 13·3 × 10^{-2} atm.
[c] p_{TO} 1·33 × 10^{-2} atm, p_A 6·7 × 10^{-2} atm.

TABLE 2. REACTIVITIES OF BENZALDHYDE AT 373° WITH CATALYST VOLUME OF 2·5 ml AND GAS SPACE VELOCITY OF 7200 hr^{-1}[a]

Reaction	Conversion of benzaldehyde (mole %)	Yield of benzonitrile (mole %)	Selectivity to benzonitrile (mole %)
Ammoxidation	53·5	53·5	100
Oxidation	3·5	—	—
Ammonolysis	53·3	21·4	40

[a] Pressures of reactants are similar to those in Table 1.

Treatment of data. Since the volume change during the reaction is negligible, the rate may be

$$v_S = -\frac{\mathrm{d}[\text{substrate}]}{\mathrm{d}t} = -\frac{\mathrm{d}\left(\dfrac{p_{SO}(1-x_S)}{RT_0}\right)}{\mathrm{d}\left(\dfrac{V}{F}\right)} = \frac{p_{SO}\,\mathrm{d}x_S}{RT_0\,\mathrm{d}\left(\dfrac{V}{F}\right)} = k_S p_S^s p_A^a p_O^o \cdots \quad (1)$$

If p_A, $p_O \ldots$ is nearly constant, integration of Eq 1 leads to

$$\frac{p_{SO}}{(1-s)}\{1-(1-x_S)^{1-s}\} = p_{SO}x_S\left\{1+\frac{s}{2}x_S+\frac{s(s+1)}{6}x_S^2+\ldots\right\}$$
$$= k'_S R T_0 p_{SO}^s\left(\frac{V}{F}\right) \quad (2)$$

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* The rate of oxidation of benzaldehyde over V_2O_5 catalysts was almost equal to that of the ammoxidation.[11]

where $k'_S = k_S p^a_A p^o_O \ldots$. If x_S is small,

$$p_{SO} x_S \simeq k'_S R T_O p^s_{SO} \left(\frac{V}{F}\right) \tag{3}$$

Hence the s value in this case can be estimated from the slope of line in a plot of $\log(p_{SO}x_S)$ vs. $\log(p_{SO})$. If $x_S \leqslant 0{\cdot}6$ and $s \simeq \frac{1}{2}$, Eq 2 is transformed to

$$p_{SO} x_S \left(1 + \frac{x_S}{4}\right) \simeq k'_S R T_O p^s_{SO} \left(\frac{V}{F}\right) \tag{4}$$

Similarly, the s value can be estimated from a slope in a plot of $\log p_{SO} x_S [1 + (x_S/4)]$ vs. $\log p_{SO}$ in Eq 4. In the same manner, the values of a and o are obtainable.

Kinetics of ammoxidation of toluene. When p_O and $p_A > p_T$, and p_O and p_A are virtually constant, the rate law and apparent energies of activation can be obtained by using Eqs 3 and 4.

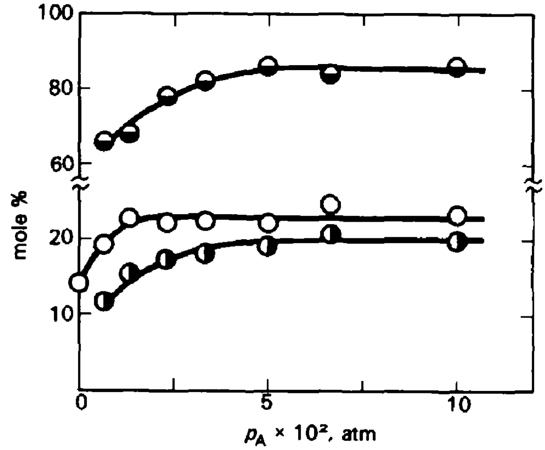

FIG. 1 Effect of partial pressure of ammonia at 400° with catalyst volume of 5·0 ml, space velocity of 3600 hr^{-1}. p_{TO} 1·33 × 10^{-2} atm and p_O 13·3 × 10^{-2} atm.
○, conversion of toluene; ◑, yield of benzonitrile; ●, selectivity to benzonitrile.

On ammoxidation of toluene, the selectivities to benzonitrile were affected by p_A. The rate of toluene consumption was constant at $p_A \geqslant 1{\cdot}3 \times 10^{-2}$ atm, but diminished at lower p_A (Fig. 1). At $p_A \geqslant 4{\cdot}7 \times 10^{-2}$ atm, the yield of benzonitrile was constant (ca. 20%), and the selectivities to benzonitrile was about 85 mole%. Therefore, under the standard composition for ammoxidation (p_{TO} 1·33 × 10^{-2} atm, p_O 13·3 × 10^{-2} atm, and p_A 6·7 × 10^{-2} atm), the rates of toluene consumption and benzonitrile formation were independent of p_A (or v_T is proportional to p^0_A).

The selectivities to benzonitrile were almost constant at p_{TO} 0·67–2·67 × 10^{-2} atm and p_O 3·3–20 × 10^{-2} atm, as shown in Table 3. Fig. 2 shows that the rate of benzonitrile formation has the same orders as the rate of toluene consumption by applying Eq. 3. Both rates are proportional to $p_T^{0{\cdot}45} p_O^{0{\cdot}45}$.

Since additions of benzonitrile, benzaldehyde (Fig. 3) and water (0·23–0·93 × 10^{-2} atm) had no effect on the rate of benzonitrile formation, the ammoxidation rate is simply expressed as

$$v_T = k_T p_T^{0{\cdot}45} p_O^{0{\cdot}45} p_A^0 \tag{5}$$

TABLE 3. EFFECT OF PARTIAL PRESSURE OF TOLUENE AT 400° WITH CATALYST VOLUME OF 2·5 ml AND SPACE VELOCITY OF 7200 hr^{-1}[a]

Partial pressure of toluene $\times 10^{-2}$ atm	Conversion of toluene (%)	Yield of benzonitrile (mole %)	Selectivity to benzonitrile (mole %)
0·67	20·4	18·2	89
1·00	16·7	15·2	91
1·33	13·6, 13·9	12·5	91
2·00	11·5, 10·8	9·8	88
2·67	9·7	8·8	91

[a] p_O 13·3 $\times 10^{-2}$ atm, p_A 6·7 $\times 10^{-2}$ atm.

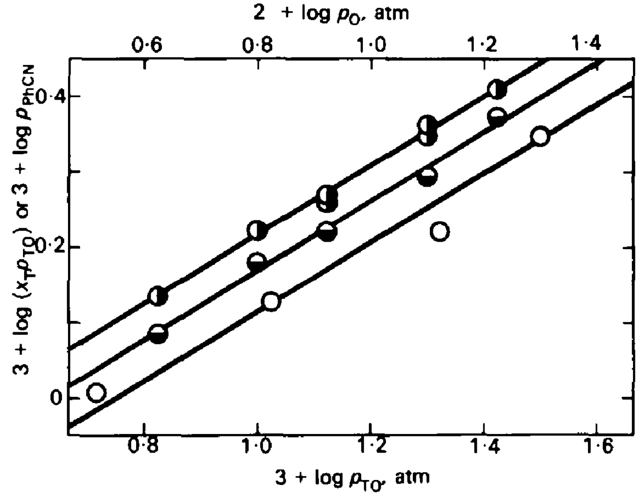

FIG. 2 Effect of partial pressure of toluene or oxygen at 400° with catalyst volume of 2·5 ml, space velocity of 7200 hr^{-1}, p_{TO} of 0·67–2·67 $\times 10^{-2}$ atm, p_O of 3·3–20 $\times 10^{-2}$ atm and p_A of 6·7 $\times 10^{-2}$ atm. ○, log p_O vs. log p_{PhCN}; ◒, log p_{TO} vs. log p_{PhCN}; ◐, log p_{TO} vs. log ($x_T p_{TO}$).

Arrhenius plots of k'_S in Eq. 4 are shown in Fig. 4, when x_S is x_T. The apparent energies of activation for toluene consumption was ca. 23 kcal/mole.

As to oxidation of toluene, the rate of toluene consumption was diminished by adding benzaldehyde or benzoic acid to the reaction system (Table 4), but water (0·33–0·93 $\times 10^{-2}$ atm) had no effect. Hence, the low value of x_T at low p_A may be due to the retardation effect of benzaldehyde or benzoic acid. Moreover, addition of benzaldehyde has no effect, since it is converted rapidly to benzonitrile under these conditions (Table 2).

The rate-determining step for the ammoxidation of toluene may be the oxidation of toluene.

Kinetics of ammoxidation and ammonolysis of benzaldehyde. The selectivities to benzonitrile in the ammoxidation of benzaldehyde were affected by p_O (Fig. 5). The rate of benzaldehyde consumption, v_B, was independent of p_O, but the yield of benzonitrile decreased with lowering p_O. This means that oxygen promotes the formation of benzonitrile from benzaldehyde-ammonia adduct. Rate v_B at p_O above

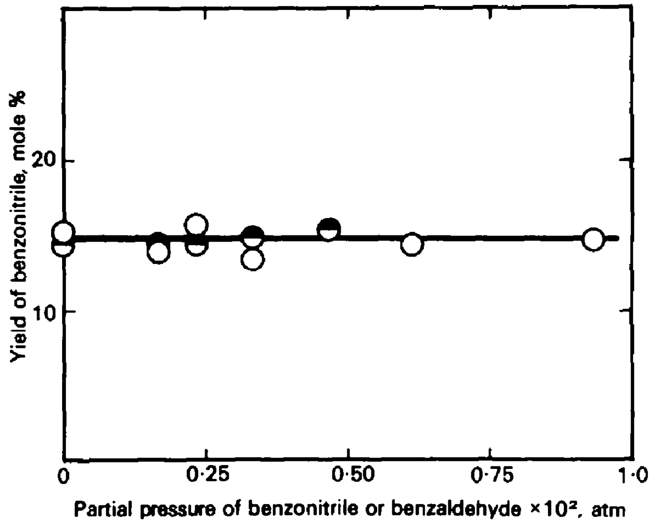

FIG. 3 Effect of addition of benzonitrile (○) or benzaldehyde (◓) at 400° with catalyst volume of 2·5 ml, space velocity of 7200 hr^{-1}, p_{T0} of 1·33 × 10^{-2} atm, p_O of 13·3 × 10^{-2} atm and p_A of 6·7 × 10^{-2} atm.

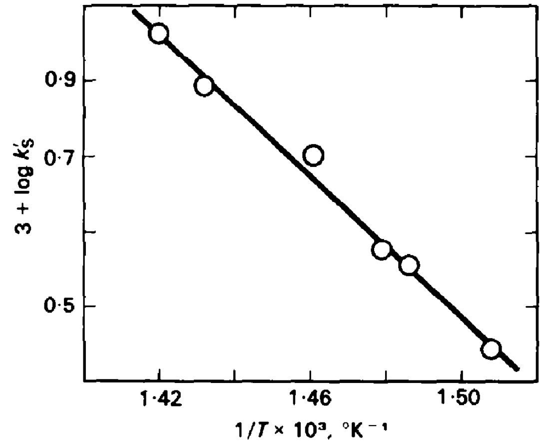

FIG. 4 Arrhenius plot of k'_S.

TABLE 4. EFFECT OF ADDITIVES ON OXIDATION OF TOLUENE AT 400° WITH CATALYST VOLUME OF 5·0 ml AND SPACE VELOCITY OF 3600 hr^{-1} [a]

Additive	Partial pressure of additive × 10^{-2} atm	Conversion of toluene (%)
None	—	21·2
Toluene	0·67	16·8
Benzaldehyde	0·67	10·7
Benzoic acid	0·67	6·2

[a] p_{T0} 1·33 × 10^{-2} atm, p_O 13·3 × 10^{-2} atm.

$6{\cdot}7 \times 10^{-2}$ atm was equal to the rate of benzonitrile formation and independent of p_O.

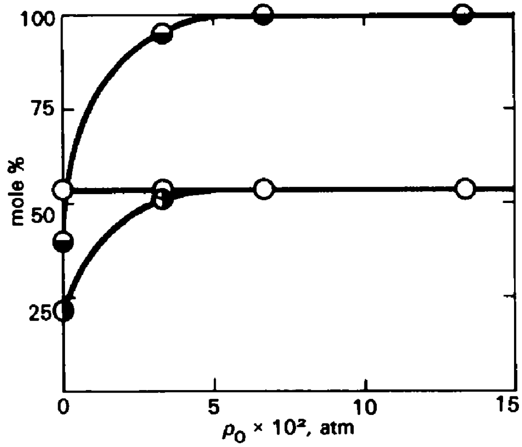

FIG. 5 Effect of partial pressure of oxygen at 373° with catalyst volume of 2·5 ml, space velocity of 7200 hr^{-1}, p_{BO} of $1{\cdot}33 \times 10^{-2}$ atm and p_A of $6{\cdot}7 \times 10^{-2}$ atm.

○, conversion of benzaldehyde; ◑, yield of benzonitrile; ⊖, selectivity to benzonitrile.

The dependences of v_B on p_B and p_A are shown in Fig. 6. The slopes of the lines give rate equation: $v = kp_B^{0{\cdot}47}p_A^{0{\cdot}42}$. Since there is no effect of added benzonitrile at $0{\cdot}4$–$1{\cdot}0 \times 10^{-2}$ atm and toluene at $1{\cdot}33 \times 10^{-2}$ atm, the ammoxidation rate of benzaldehyde is expressed as:

$$v_B = k_B p_B^{0{\cdot}47} p_A^{0{\cdot}42} p_O^0 \tag{6}$$

Arrhenius plot for k_S' in Eq. 4 is shown in Fig. 7, when x_S is x_B, the apparent energy of activation being ca. 11 kcal/mole.

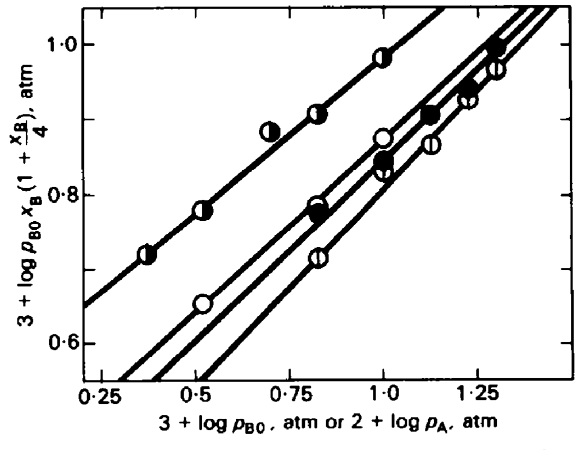

FIG. 6 Effect of p_B (●) or p_A (◑) on ammoxidation ($p_O = 1{\cdot}33 \times 10^{-2}$ atm) and p_B (⦶) or p_A (○) on ammonolysis of benzaldehyde at 373° with catalyst volume of 2·5 ml, space velocity of 7200 hr^{-1}, p_{BO} of $0{\cdot}67$–$2{\cdot}00 \times 10^{-2}$ atm and p_A $2{\cdot}33$–$10{\cdot}0 \times 10^{-2}$ atm.

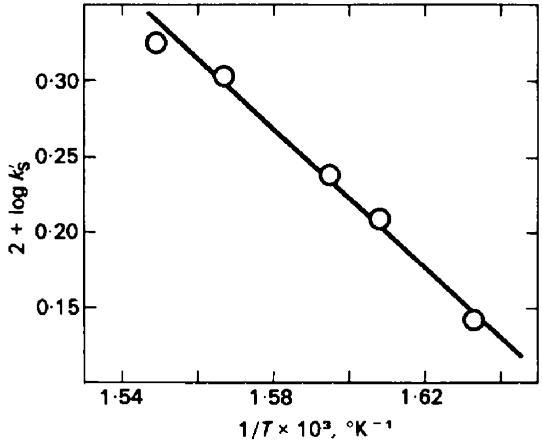

FIG. 7 Arrhenius plot of consumption of benzaldehyde.

The rate for ammonolysis of benzaldehyde (Fig. 6) are expressed as:

$$v'_B = k_B p_B^{0.53} p_A^{0.44} \tag{7}$$

The similarity of the exponents of p_B and p_A in both reactions (Eqs 6 and 7) suggests that they have a common rate-determining step.

Explanation by means of the Langmuir-Hinshelwood mechanism. In ammoxidation of toluene, the chemical reactions on catalyst surface determine the rate. The Langmuir–Hinshelwood mechanism, involving a rate-determining reaction between the adsorbed molecules, and the Markham–Benton equation,[12] for the adsorption isotherms may be applied.

$$\theta_i = K_i p_i/(1 + \sum_i K_i p_i) \tag{8}$$

The effects of additives on ammoxidation and oxidation of toluene and that on ammoxidation of benzaldehyde indicate that the order in adsorption ability is $PhCO_2H > PhCHO > PhCH_3 > PhCN, H_2O, O_2$. Adsorption sites may be (i) a site which adsorbes aromatics strongly but oxygen weakly in a dissociated form. On this site, the order of adsorption equilibrium constants is supposed to be $K_{PhCO_2H} > K_B > K_T > K_{PhCN}$, K_O and K_{H_2O}. (ii) Another site adsorbs ammonia strongly but other gases weakly. Surface coverages of starting materials are expressed as:

$$\theta_T = K_T p_T/[1 + K_T p_T + K_B p_B + \sqrt{(K_O p_O)} + \sum_i K_i p_i) \tag{9}$$

$$\theta_B = K_B p_B/[1 + K_T p_T + K_B p_B + \sqrt{(K_O p_O)} + \sum_i K_i p_i) \tag{10}$$

$$\theta_O = \sqrt{(K_O p_O)}/[1 + K_T p_T + K_B p_B + \sqrt{(K_O p_O)} + \sum_i K_i p_i) \tag{11}$$

$$\theta_A = K_A p_A/(1 + K_A p_A + \sum_j K_j p_j) \tag{12}$$

where *i* and *j* mean any miscellaneous products.

As stated above, ammoxidation of toluene has a rate-determining step between adsorbed oxygen and adsorbed toluene, hence $v_T \propto \theta_T\theta_O$.* Since K_Tp_T and $\sqrt{(K_O0_O)} > K_Bp_B + \sum_i K_ip_i$ under these conditions,

$$v_T = k_T^0\theta_T\theta_O \simeq k_T^0\frac{K_Tp_T\sqrt{K_Op_O}}{(1 + K_Tp_T + \sqrt{K_Op_O})^2} \tag{13}$$

Similarly, v_B in ammoxidation of benzaldehyde and v'_B for ammonolysis of benzaldehyde are proportional to $\theta_B\theta_A$, because the rate-determining step is the reaction between adsorbed benzaldehyde and adsorbed ammonia. Since $K_Bp_B > K_Tp_T + \sqrt{(K_Op_O)} + \sum_i K_ip_i$ in Eq 10, and $K_Ap_A > \sum_j K_jp_j$ in Eq 12 under these conditions,

$$v_B \text{ or } v'_B = k_B^0\theta_B\theta_A \simeq k_B^0\frac{K_Bp_B}{1 + K_Bp_B}\frac{K_Ap_A}{1 + K_Ap_A} \tag{14}$$

Assuming[14] empirical Eq 15, Eqs 13 and 14 are recast into Eqs 16 and 17:

$$\frac{1}{1 + K_Tp_T + \sqrt{K_Op_O}} \simeq \frac{1}{1 + K_Tp_T}\cdot\frac{1}{1 + \sqrt{K_Op_O}} \text{ and } \frac{K_ip_i}{1 + K_ip_i} \simeq C_i(K_ip_i)^i \tag{15}$$

C_i: proportionality constant

$$v_T \propto p_T^{2t-1}p_O^{2o-0\cdot5} \tag{16}$$

$$v_B \text{ or } v'_B \propto p_B^bp_A^a \tag{17}$$

The values, t = 0·73, o = 0·48, b = 0·47 − 0·53 and a = 0·42 − 0·44, are obtained from Eqs 5, 6 and 7. These values indicate that the order of the adsorption equilibrium constant is $K_B > K_T \gg K_O$, that oxygen is adsorbed in a dissociated form, and that ammonia is adsorbed strongly on the other sites.

Moreover, Eqs 3 and 13 give approximation of v_T:

$$v_T \simeq \frac{p_{T0}x_T}{RT_0(V/F)} \simeq k_T^0\frac{K_Tp_{T0}\sqrt{(K_Op_O)}}{(1 + K_Tp_{T0} + \sqrt{K_Op_O})^2} \tag{18}$$

As shown in Fig. 8, plots of $x_T^{-1/2}$ vs. p_{T0} and $p_O^{1/4}x_T^{-1/2}$ vs. $p_O^{1/2}$ give the values of $k_T^0RT_0$, K_T and K_O at 400° to be $6{\cdot}2 \times 10^2$ atm hr^{-1}, 29·0 atm^{-1} and 0·15 atm^{-1}, respectively. Similarly, v_B and v'_B are obtained from Eq 14:

$$v_B \text{ or } v'_B = -\frac{dp_B}{RT_0\,d(V/F)} \simeq k_B^0\frac{K_Bp_B}{1 + K_Bp_B}\quad\frac{K_Ap_A}{1 + K_Ap_A} \tag{19}$$

Integration of Eq 19 leads to linear relationships between $\ln(p_{B0}/p_B)$ vs. $(p_{B0} - p_B)$, and $\{\ln(p_{B0}/p_B) + k_B(p_{B0} - p_B)\}^{-1}$ vs. p_{A0}^{-1} (Figs 9 and 10). These relationships afford the values of $1{\cdot}3 \times 10^2$ atm hr^{-1} for $k_B^0RT_0$, $1{\cdot}52 \times 10^2$ atm^{-1} for K_B and 27·2 atm^{-1} for K_A with ammoxidation at 373°, and $1{\cdot}2 \times 10^2$ atm hr^{-1} for $k_B^0RT_0$, $1{\cdot}43 \times 10^2$ atm^{-1} for K_B and 36·6 atm^{-1} for K_A with ammonolysis at 373°. Therefore, the order $K_B > K_A \simeq K_T \gg K_O$, agrees to the order in the above assumption.

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* The oxidation of CO over Cr_2O_3 may be considered similarly.[13]

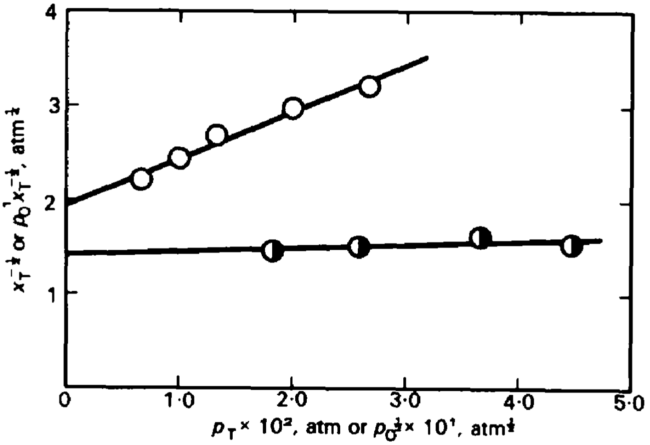


FIG. 8 Calculation of K_T and K_O in ammoxidation of toluene.
○, p_{T0} vs. $x_T^{-1/2}$
◐, $p_O^{1/2}$ vs. $p_O^{1/2} x_T^{-1/2}$

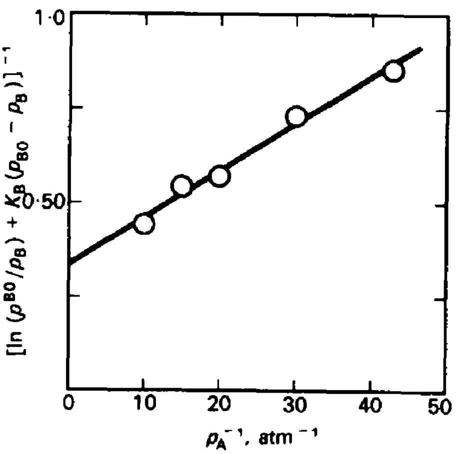


FIG. 9 Calculation of K_A in ammonolysis of benzaldehyde.

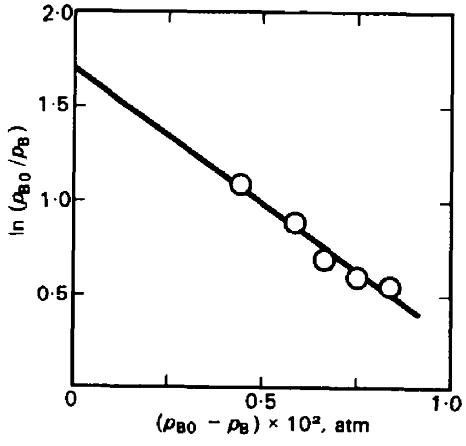


FIG. 10 Calculation of K_B in ammonolysis of benzaldehyde.

Intermediate for nitrile formation. Following mechanisms are considerable for the formation of nitrile from aldehyde.

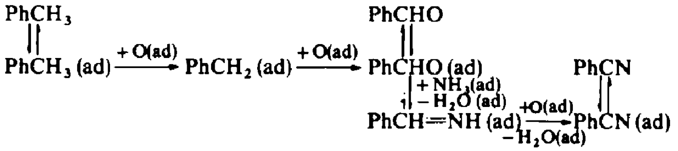
$$\text{RCHO} \xrightarrow{\text{O}} \text{RCO}_2\text{H} \xrightarrow{\text{NH}_3} \text{RCONH}_2 \xrightarrow{-\text{H}_2\text{O}} \text{RCN} \qquad (20a)^{5,8}$$

$$\text{RCHO} \xrightarrow{-\text{H}} \text{R}\dot{\text{C}}\text{O} \xrightarrow{\text{NH}_3} \text{RCONH}_2 \xrightarrow{-\text{H}_2\text{O}} \text{RCN} \qquad (20b)^{15}$$

$$\text{RCHO} \xrightarrow{\text{NH}_3} [\text{RCHO}\cdot\text{NH}_3] \xrightarrow{-\text{H}_2\text{O}} \text{RCH=NH} \xrightarrow{-\text{H}} \text{RCN} \qquad (20c)^{5,11,16}$$

$$\text{RCHO} \xrightarrow{\text{NH}_3} [\text{RCHO}\cdot\text{NH}_3] \xrightarrow{-\text{H}} \text{RCONH}_2 \xrightarrow{-\text{H}_2\text{O}} \text{RCN} \qquad (20d)^{17}$$

where R means alkenyl or aryl group. Pathways 20a and b seem to be unimportant with Cr_2O_3 catalyst, since the rate of oxidation is much slower than that of ammoxidation (Table 2). A common intermediate $RCHO\cdot NH_3$ or probably α-aminoalcohol in 20c and d may react via either dehydration (20c) or dehydrogenation (20d). In the case of nickel peroxide,[18] the dehydration to nitrile is predominant at above room temperature, but dehydrogenation to amide is favored at below room temperature, while I_2,[19] copper compounds with oxygen gas,[20] $KMnO_4$,[21] MnO_2,[21] Ag_2O[21] and $Pb(OAc)_4$[22] as oxidants gave little or no benzamide. In the gaseous reaction of benzaldehyde and ammonia, dehydration of α-aminoalcohol is rapid and the catalyst is effective for dehydrogenation of aldimine to give nitrile.[23] Therefore, the dehydration is faster than dehydrogenation and 20c is more important. The tarry material formed in the absence of oxygen, i.e. in ammonolysis, may be polymerized aldimine.[24] Hence a main route of ammoxidation over a chromium oxide catalyst should be expressed as Scheme 1.



SCHEME 1. Main route of ammoxidation of toluene over a chromium oxide catalyst.

Probable mechanism of ammoxidation. The oxygen molecules adsorbed on catalyst act as electron-acceptors, while various hydrocarbon molecules act as electron-donors.[25] The following steps have been proposed for the adsorption on Cr_2O_3 catalyst,[26] where (ad) means adsorbed gas on catalyst.

$$\text{O}_2 + \text{catalyst} \rightarrow \text{O}_2^-(\text{ad}) + \oplus \qquad (21)$$

$$\text{O}_2^-(\text{ad}) + \text{catalyst} \rightarrow 2\text{O}^-(\text{ad}) + \oplus \qquad (22)$$

where ⊕ means a positive hole. The adsorption is predominant as O_2^- below 300°, but as O^- above 300°. Therefore, the mechanism of ammoxidation may be as follows, where (ad) mean adsorbed.

$$\text{PhCH}_3 + \oplus \rightleftharpoons \text{PhCH}_3^+(\text{ad}) \qquad (23)$$

$$\text{O}_2 \rightleftharpoons 2\text{O}^-(\text{ad}) + 2\oplus \qquad (24)$$

$$\text{PhCH}_3^+(\text{ad}) + \text{O}^-(\text{ad}) \rightleftharpoons [\text{PhCH}_3^+(\text{ad})\text{O}^-(\text{ad})] \qquad (25)$$

$$[\text{PhCH}_3^+(\text{ad})\text{O}^-(\text{ad})] \rightarrow \text{PhCH}_2\cdot(\text{ad}) + \text{OH}(\text{ad}) \qquad (26)$$

$$PhCH_2\cdot(ad) + O^-(ad) \rightleftharpoons [PhCH_2\cdot(ad)O^-(ad)] \rightarrow PhCHO(ad) + e + \cdot H(ad) \quad (27)$$

$$\cdot H(ad) + \cdot OH(ad) \rightarrow H_2O(ad) \rightleftharpoons H_2O \quad (28)$$

$$PhCHO \rightleftharpoons PhCHO(ad) \quad (29)$$

$$NH_3 \rightleftharpoons NH_3(ad) \quad (30)$$

$$PhCHO(ad) + NH_3(ad) \rightleftharpoons [PhCHO(ad)NH_3(ad)] \quad (31)$$

$$[PhCHO(ad)NH_3(ad)] \rightleftharpoons PhCH{=}NH(ad) + H_2O(ad) \quad (32)$$

$$PhCH\ldots NH(ad) + O^-(ad) \rightarrow PhCN(ad) + H_2O(ad) + e \quad (33)$$

$$PhCN \rightleftharpoons PhCN(ad) \quad (34)$$

The rate-determining step may be Eq 26 in ammoxidation of toluene, and Eq 31 or 32 in ammoxidation of benzaldehyde.

The higher selectivity to benzonitrile over Cr_2O_3, compared with that over V_2O_5, may be explained as follows: The main pathway for ammoxidation of aromatic hydrocarbons over V_2O_5 may be 20a as mentioned above. The decomposition and the complete oxidation of the partially oxidized products occurs owing to the strong oxidizing ability of catalysts, hence the yield of nitrile is relatively low. In fact, the selectivities to nitrile increase at lower[5,27] p_O or x_S and by using catalyst additives like K_2SO_4 which suppresses the complete oxidation.[9] On the other hand, low yield of carbon oxides with Cr_2O_3 catalyst indicates that complete oxidation is suppressed by the lower activity for oxidation of this catalyst. Therefore, the selectivity to benzonitrile is higher.

EXPERIMENTAL

Materials. Guaranteed reagent grade toluene was purified by successive shaking with H_2SO_4, $NaHCO_3$ and water, followed by drying over Na and then distillation (b.p. 110·6°, n^{20° 1·4971). C.p. grade benzaldehyde was purified by shaking with 5% Na_2CO_3aq, followed by drying over $CaCl_2$ and then vacuum-distilled under N_2 (b.p. 54·5–55·0°/6–7 mm Hg). Benzonitrile was purified by distillation over P_2O_5 (b.p. 190°). Commercial ammonia, N_2 and O_2 were employed.

Preparation of catalyst. Activated alumina (8–14 mesh), obtained from Wako Pure Chem. Ind. Ltd., was impregnated with $(NH_4)_2Cr_2O_7$aq containing 0·5 mg atom Cr/Al_2O_3 g, dried and heated at 150° for 3 hr and then calcinated in air at 550° for 3 hr. The calcinated catalyst was aged under the reaction conditions for 20 hr before use. The activities are stable in a series of experiments.

Apparatus and procedures. The reaction was carried out in a flow system at atm press, and gas chromatograph, connected to the experimental apparatus, was used for product analysis (Fig. 11). A reactor of hard glass, 17 mm i.d. with a concentric thermowell (5 mm o.d.), was immersed in a thermostated lead bath. Toluene, benzaldehyde, benzonitrile, benzoic acid and water were taken from vaporizers, immersed in a thermostated water or polyethyleneglycol (Mol. Wt. 400) bath, and passed with N_2 into the reactor. A mixture of gas, consisted of known amounts of N_2, O_2, ammonia, a substrate and additive, was passed through the reactor. After a steady-state in the system has been attained, exit gas was sampled out by a 5 ml sampler for the analysis of aromatic compounds, and also by a 2 ml injector for the analysis of gaseous products. Aromatic and gaseous compounds in the exit gas were determined by gas chromatography. A column of 25 wt% paraffin wax on Chamelite CK 40 cm, column I, was used for toluene and benzonitrile, a column of 30 wt% PEG # 6000 on Celite 545 50 cm (column I) for benzaldehyde and benzonitrile, a silica gel column 100 cm (column II) for CO_2, and a molecular sieve 5A column 185 cm (column III) for O_2, N_2 and CO.

Nomenclature. A, Ammonia; B, Benzaldehyde; O, Oxygen; S, Substrate, i.e. benzaldehyde or toluene; T, Toluene; a, b, o, s, t, kinetic orders in A, B, O, S and T, respectively; p_A, p_B, p_O, p_S, p_T, partial pressures of subscripted substance; p_{BO}, p_{SO}, p_{TO}, initial partial pressures of subscripted substances; v_S, rate of consumption of subscripted substance on ammoxidation, mole ml^{-1} hr^{-1}; v'_S, rate of consumption of subscripted substance on ammonolysis, mole ml^{-1} hr^{-1}; k_S, rate constant of reaction of substrate; k_S^0, rate constant of reaction of substrate on catalyst surface; x_S, conversion of substrate, mole ml^{-1}; y, yield of benzonitrile, mole mol^{-1}; θ_i, surface coverage of i gas; K_i, adsorption equilibrium constant of i gas, atm^{-1}; V, volume of catalyst, ml; F, flow rate of gas (STP), ml hr^{-1}.

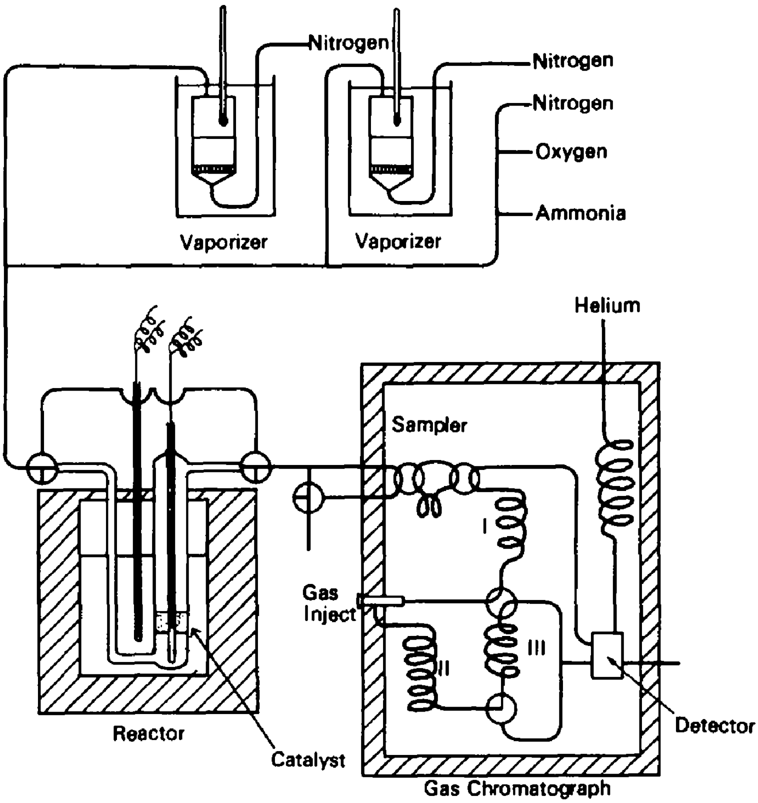


FIG. 11 Flow diagram of apparatus.

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REFERENCES

[1] U.S. P. 2,499,055 (1950); 2,828,325 (1958); 2,838,558 (1958); Brit. P. 796,765 (1958); 796,766 (1958); 806,492 (1958); 807,485 (1959); 809,704 (1959); Belg. P. 632,702 (1963).

[2] Fr. P. 1,368,494 (1964); *Chem. Eng. Prog.* **60**, (9) 48 (1964).

[3] K. Sato, J. Kato and N. Ohta, *Kogyo Kagaku Zasshi* **70**, 1160 (1967).

[4] Y. Ogata and K. Sakanishi, *The Meeting of the Tokai Branch of the Chemical Society of Japan*, Nagoya, Nov (1966).

[5] Y. Ogata, Y. Sawaki and K. Sakanishi, *Kogyo Kagaku Zasshi* **67**, 1542 (1964).

[6] H. Tanabe, F. Araki and H. Kobayashi, *The 5th Symposium of the Reaction Engineering of Japan*, Tokyo, Oct. (1965).

[7] M. Ito and K. Sano, *Yuki Gosei Kagaku Kyokaishi* **25**, 329 (1967).

[8] D. J. Hadley, *Chem. & Ind.* 238 (1961).

[9] Y. Ogata and K. Sakanishi, *Kogyo Kagaku Zasshi* **69**, 2294 (1966).

[10] M. Ito, *Yuki Gosei Kagaku Kyokaishi* **25**, 337 (1967); M. Ito and K. Sano, *Bull. Chem. Soc. Japan* **40**, 1307, 1315, 1321 (1967).

[11] S. Saito and N. Ohta, *Yuki Gosei Kagaku Kyokaishi* **22**, 730 (1964).

[12] E. C. Markham and A. F. Benton, *J. Am. Chem. Soc.* **53**, 497 (1931).

[13] K. Tamara, S. Teranishi and K. Hattori, *Kogyo Kagaku Zasshi* **63**, 714 (1960).

[14] J. E. Benson and T. Kwan, *J. Phys. Chem.* **60**, 1601 (1956).

[15] B. V. Suvorov, S. R. Rafikov A. D. Kagarlitskii and V. S. Kudinova, *Neftekhim. Akad. Nauk Turkm. SSR* 253 (1963); S. R. Rafikov, D. Kh. Sembaev and B. V. Suvorov, *Zh. Obshch. Khim.* **32**, 839 (1962).

[16] W. F. Brill and J. H. Finely, *Ind. & Chem., Product Research & Development* Vol. 3; No. 2; p. 89 (1964).

[17] T. Kita, *Prepublication of the Symposium of the Oxidation Reaction* p. 66. Tokyo, Dec. (1966).

[18] K. Nakagawa, H. Onoe and K. Minami, *The 19th Annual Meeting of the Chemical Society of Japan*, 3N221 (1966).

[19] A. Misono, T. Osa and S. Koda, *Bull. Chem. Soc. Japan* **39**, 854 (1966).

[20] W. Brackman and P. J. Smit, *Rec. Trav. Chim.* **82**, 757 (1963); E. Fischer, *J. Prakt. Chem.* **29**, 199 (1965); A. Misono, T. Osa and S. Koda, *Bull. Chem. Soc. Japan* **40**, 912 (1967).

[21] A. Misono, T. Osa, S. Koda and Y. Sato, *Bull. Chem. Soc. Japan* **40**, 1553 (1967).

[22] K. N. Parameswaran and O. M. Friedman, *Chem. & Ind.* 988 (1965).

[23] S. Saito and N. Ohta, *Yuki Gosei Kagaku Kyokaishi* **22**, 472 (1964).

[24] T. L. Tolbert and B. Houston, *J. Org. Chem.* **28**, 695 (1963).

[25] L Ya. Margolis, *Advances in Catalysis* **14**, 429 (1963).

[26] K. Tarama, S. Teranishi and K. Hatori, *Nippon Kagaku Zasshi* **81**, 1665 (1960).

[27] A. Uchida, Y. Asaoka and S. Matsuda, *Kogyo Kagaku Zasshi* **68**, 300 (1965).