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

K. SAKANISHI and Y. OGATA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Nagoya, Japan

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Abstract—The kinetics of the catalytic vapor-phase ammoxidation of ethylbenzene over a chromium oxide catalyst have been studied in a flow system at atmospheric pressure. Styrene and benzonitrile were the main products in the ammoxidation of ethylbenzene, but neither acetophenone nor benzyl cyanide was detectable. The rate of ammoxidation of ethylbenzene is expressed as: $k[\mathrm{PhCH_2CH_3}]^{0\cdot73}[\mathrm{O_2}]^{0\cdot39}$, while the rate of formation of styrene as: $k[\mathrm{PhCH_2CH_3}]^{0\cdot78}[\mathrm{O_2}]^{0\cdot25}$ and that of the formation of benzonitrile as: $k[\mathrm{PhCH_2CH_3}]^{0\cdot55}[\mathrm{O_2}]^{0\cdot90}$. All these rates are almost independent of the concentrations of ammonia. The apparent activation energy for the ammoxidation of ethylbenzene is ca. 23 kcal/mole. The rate of ammoxidation of styrene is expressed as: $k[\mathrm{PhCH{=}CH_2}]^{-0\cdot10}[\mathrm{O_2}]^{0\cdot50}$, and independent of the concentrations of ammonia. These results suggest that styrene is formed by the reaction between the adsorbed ethylbenzene and the adsorbed oxygen in a dissociated form (i.e. oxidative dehydrogenation), and that the main pathway for the ammoxidation of ethylbenzene is a consecutive reaction: $\mathrm{PhCH_2CH_3} \rightarrow \mathrm{PhCH{=}CH_2} \rightarrow \mathrm{PhCN}$. The rate equations of the formation of styrene and benzonitrile and the effect of the addition of styrene were interpreted in terms of the Langmuir–Hinshelwood mechanism. The rate constants (k°) for the reaction of substrates on the catalyst surface and the adsorption equilibrium constants of reactant gases (K) were compared with those in the ammoxidation of toluene.

IN a previous paper,[1] we suggested a pathway for the ammoxidation of toluene over chromium oxide ($\mathrm{Cr_2O_3}$) which involved benzaldehyde and benzylidenimine and we explained the rate data by means of the Langmuir–Hinshelwood mechanism. We found that styrene and benzonitrile are the main products in the ammoxidation of ethylbenzene over $\mathrm{Cr_2O_3}$–$\mathrm{Al_2O_3}$ or $\mathrm{V_2O_5}$–$\mathrm{K_2SO_4}$–$\mathrm{Al_2O_3}$,[2] while it has been reported that no styrene was detected in the ammoxidation of ethylbenzene over $\mathrm{V_2O_5}$ catalyst.[3] The formation of styrene has been observed in the oxidation of ethylbenzene over Fe–Mo and Co–Mo catalysts,[4] and it may be related to the oxidative dehydrogenation of n-butenes to butadiene.[5,6] As little data have been presented on the kinetics of ammoxidation of ethylbenzene, an attempt has been made to clarify the mechanistic feature of the ammoxidation and oxidative dehydrogenation of ethylbenzene over $\mathrm{Cr_2O_3}$ in terms of the kinetics for the reactions of ethylbenzene and the intermediary styrene, the effects of additives and the Langmuir–Hinshelwood mechanism.

RESULTS

The nomenclature of symbol letters used has been given in the last section.

The mass transfer effect on the rate was examined at a fixed gas space velocity

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(3600 hr^{-1}) for ammoxidation of ethylbenzene at the standard composition of reactant gas (p_E 1·33 × 10^{-2} atm, p_O 13·3 × 10^{-2} atm, and p_A 6·7 × 10^{-2} atm) and 389°. As the conversion of ethylbenzene and yields of styrene and benzonitrile were almost constant (24·3%, 16·5% and 7·6%, respectively) at a catalyst volume of 2·5–5·0 ml, the rate is determined by the reaction on catalyst surface.

Styrene, benzonitrile, hydrogen cyanide, water and trace amounts of CO_2 were formed in the ammoxidation of ethylbenzene over Cr_2O_3, and detectable amounts of benzene and toluene (below 0·05%), but no acetophenone and benzyl cyanide were formed. A trace of styrene was formed in the reaction of ethylbenzene over Cr_2O_3 in a N_2 stream or in a NH_3—N_2 stream (i.e. ammonolysis of ethylbenzene), while considerable amounts of styrene were formed in the oxidation of ethylbenzene at low p_O (2 × 10^{-2} atm). Since the presence of oxygen in the reaction system is necessary for the formation of styrene from ethylbenzene, the formation of styrene may be oxidative dehydrogenation. Benzonitrile, hydrogen cyanide, water and CO_2 were formed in the ammoxidation of styrene. The results of ammoxidation of ethylbenzene and styrene at the standard composition of reactant gas are shown in Table 1.

TABLE 1. CONDITIONS AND PRODUCTS OF AMMOXIDATIONS OF ETHYLBENZENE AND STYRENE AT 400

Substrate	Gas space velocity	Conversion of substrate[a]	Conversion of substrate to			
			PhCN[a]	HCN[a]	PhCH=CH$_2$[a]	CO$_2$[b]
Ethylbenzene	7200 hr^{-1}	0·212	0·048	0·041	0·164	trace
Styrene	3600 hr^{-1}	0·116	0·077	0·077	—	0·039

[a] Moles per mole of substrate.

[b] Based on carbons of substrate.

The treatment of experimental data was the same as previously reported,[1] i.e. the rate is expressed as:

$$v_E = -\frac{d[\text{ethylbenzene}]}{dt} = -\frac{d\left(\frac{p_{E0}(1-x_E)}{RT_0}\right)}{d\left(\frac{V}{F}\right)} = k_E p_E{}^e p_A{}^a p_O{}^n \tag{1}$$

Since $p_O > p_E$ and $p_A > p_E$, and p_O and p_A are virtually constant under experimental conditions,

$$p_{E0}x_E \simeq k_E R T_0 p_{E0}{}^e p_A{}^a p_O{}^n \left(\frac{V}{F}\right) \tag{2}$$

Hence, the rate law and apparent energy of activation can be obtained from Eq. 2.

On the ammoxidation of ethylbenzene, the rate of ethylbenzene consumption is proportional to $p_E{}^{0.73} p_O{}^{0.39}$ and independent of p_A (or proportional to $p_A{}^0$), as shown in Fig. 1.

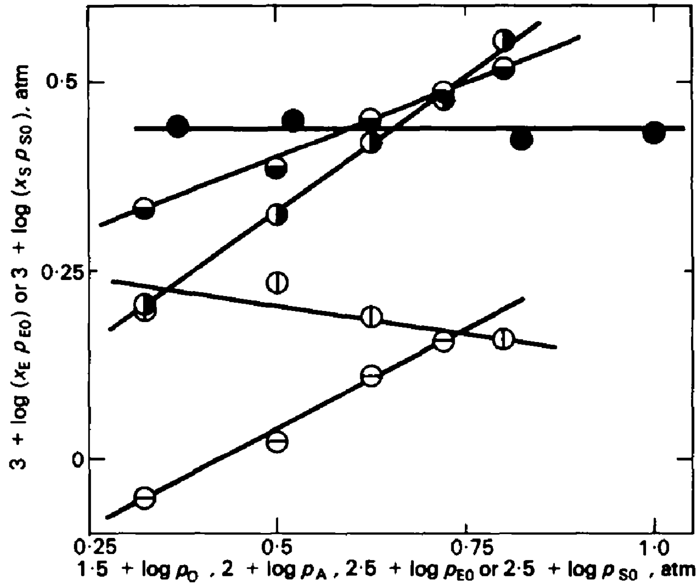


FIG. 1 Effect of p_O (◒), p_A (●) or p_{EO} (◑) in ammoxidation of ethylbenzene at 400° with catalyst of 2·5 ml and space velocity of 7200 hr^{-1}, and effect of p_O (⊖) or p_{SO} (⦶) in ammoxidation of styrene at 400° with catalyst volume of 5·0 ml and space velocity of 3600 hr^{-1}.

Similarly, the rate laws for the formation of benzonitrile and styrene are obtainable by using Eq. 2, and their rates are $p_E^{0\cdot55}p_O^{0\cdot90}$ and $p_E^{0\cdot78}p_O^{0\cdot25}$, respectively; both rates are almost constant with varying p_A, as shown in Fig. 2.

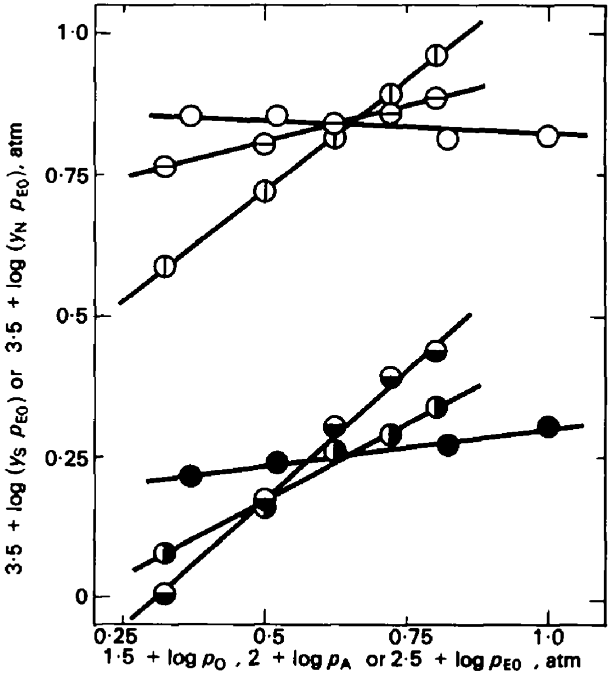


FIG. 2 Effect of p_O (⊖), p_A (○) or p_{EO} (⦶) on the formation of styrene and effect of p_O (◒), p_A (●) or p_{EO} (◑) on the formation of benzonitrile at 400° with catalyst volume of 2·5 ml and space velocity of 7200 hr^{-1}.

Addition of styrene to the reaction system in the ammoxidation of ethylbenzene diminished the rate of ethylbenzene consumption, but addition of benzonitrile or water had no effect as shown in Fig. 3. However, since the retardation effect of the styrene formed is negligible at the initial stage of reaction (or low x_E), the ammoxidation rate of ethylbenzene may be expressed as:

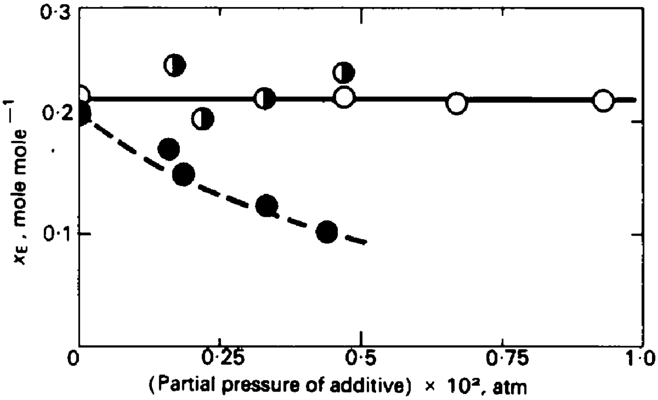


FIG. 3 Effect of addition of water (○), benzonitrile (◑) or styrene (●), and the calculated line of the retarding effect of added styrene (dotted line) at 400° with catalyst volume of 2·5 ml, space velocity of 7200 hr^{-1}, p_{E0} of 1·33 × 10^{-2} atm, p_O of 13·3 × 10^{-2} atm and p_A of 6·7 × 10^{-2} atm.

$$v_E = k_E p_E^{0 \cdot 73} p_O^{0 \cdot 39} p_A^{0} \qquad (3)$$

The rate of styrene consumption in the ammoxidation of styrene is proportional to $p_S^{-0 \cdot 10} p_O^{0 \cdot 50}$ as shown in Fig. 1, and it is independent of p_A.

Arrhenius plots of k_E and k_S are shown in Fig. 4. The apparent energies of activation for the ethylbenzene consumption and for the styrene consumption in their ammoxidation were ca. 23 and ca. 35 kcal/mole, respectively.

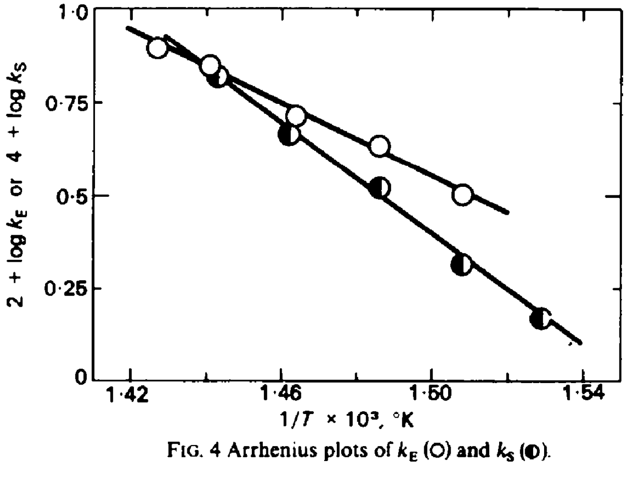


FIG. 4 Arrhenius plots of k_E (○) and k_S (◐).

The yields of benzonitrile (4·3–4·8%) in the ammoxidation of ethylbenzene were comparable with those (3·7–4·6%) in the ammoxidation of styrene under similar conditions (400°, 7200 hr^{-1} and the standard composition of reactant gas). The ratios of yields of styrene vs. benzonitrile at 7200 hr^{-1} and 400° were ca. 1·8 times as large as those at 3600 hr^{-1} and 389° with a definite composition of reactant gas (p_{E0} 0·67–2·00 $\times 10^{-2}$ atm, p_A 6·7 $\times 10^{-2}$ atm and p_O 13·3 $\times 10^{-2}$ atm). The rate of formation of benzonitrile was proportional to $p_O{}^{0\cdot 90}$, while the rate of ethylbenzene consumption was proportional to $p_O{}^{0\cdot 39}$ and the rate of formation of styrene to $p_O{}^{0\cdot 25}$ as mentioned above. The rates of formation of hydrogen cyanide were almost equal to those of benzonitrile. These results indicate that benzonitrile may be formed from styrene, and that a main pathway for the ammoxidation of ethylbenzene may be a consecutive reaction:

$$\text{PhCH}_2\text{CH}_3 \rightarrow \text{PhCH{=}CH}_2 \rightarrow \text{PhCN} + \text{HCN}$$

As stated above, the reaction on the catalyst surface determines the rate of the ammoxidation of ethylbenzene. The Langmuir–Hinshelwood mechanism, involving a rate-determining reaction between the adsorbed molecules, and Eq. 4, i.e. the Markham–Benton equation,[7] for the adsorption isotherms may be applied.

$$\theta_i = K_i p_i/(1 + \sum_i K_i p_i) \tag{4}$$

As described in our previous paper,[1] adsorption may be on (i) a site which adsorbs aromatics strongly but oxygen weakly in a dissociated form, or (ii) a site which strongly adsorbs only ammonia. The effects of additives on the ammoxidation of ethylbenzene suggest that the order of adsorption equilibrium constants is $K_S > K_E > K_{\text{PhCN}}$, K_O and K_{H_2O}, on the former site. Surface coverages of starting materials are expressed as:

$$\theta_E = K_E p_E/\{1 + K_E p_E + K_S p_S + \sqrt{(K_O p_O)} + \sum_i K_i p_i\} \tag{5}$$

$$\theta_S = K_S p_S/\{1 + K_E p_E + K_S p_S + \sqrt{(K_O p_O)} + \sum_i K_i p_i\} \tag{6}$$

$$\theta_O = \sqrt{(K_O p_O)}/\{1 + K_E p_E + K_S p_S + \sqrt{(K_O p_O)} + \sum_i K_i p_i\} \tag{7}$$

where i means any miscellaneous product.

The following inequality may exist in Eqs 5 and 7 at an early stage of ammoxi-determining reaction between adsorbed oxygen and adsorbed ethylbenzene, hence $v_E \propto \theta_E\theta_O$. Similarly, v_S in ammoxidation of styrene is proportional to $\theta_S\theta_O$.

$$v_E = k_E^0\theta_E\theta_O \tag{8}$$

$$v_S = k_S^0\theta_S\theta_O \tag{9}$$

The following inequalities may exist in Eqs 5 and 7 at an early stage of ammoxidation of ethylbenzene (i.e. low x_E and p_S).: $p_E \simeq p_{E0}$ and $K_E p_E + \sqrt{(K_O p_O)} > K_S p_S + \sum_i K_i p_i$. Therefore, Eqs 2, 5, 7 and 8 give approximation of v_E:

$$v_E \simeq \frac{p_{E0}x_E}{RT_0\left(\frac{V}{F}\right)} \simeq k_E^0\frac{K_E p_{E0}\sqrt{(K_O p_O)}}{\{1 + K_E p_{E0} + \sqrt{(K_O p_O)}\}^2} \tag{10}$$

Plots of $x_E^{-\frac{1}{2}}$ vs. p_{EO} and $p_O^{\frac{1}{2}}x_E^{-\frac{1}{2}}$ vs. $p_O^{\frac{1}{2}}$ give the values of $k_E^0RT_0$, K_E and K_O, as shown in Fig. 5. Similarly, in the ammoxidation of styrene, $p_S \simeq p_{SO}$, $p_E = 0$ and $K_Sp_S + \sqrt{(K_Op_O)} > \sum_i K_ip_i$, in Eqs 6 and 7. Eqs 2, 6, 7 and 9 give approximation of v_S:

$$v_S \simeq \frac{p_{SO}x_S}{RT_0\left(\frac{V}{F}\right)} \simeq k_S^0 \frac{K_Sp_{SO}\sqrt{K_Op_O}}{\{1 + K_Sp_{SO} + \sqrt{(K_Op_O)}\}^2} \tag{11}$$

Since $K_O = 0{\cdot}25$ atm^{-1}, plots of $x_S^{-\frac{1}{2}}$ vs. p_{SO} give the value of $k_S^0RT_0$ and K_S as shown in Fig. 5. These values are reasonable in the light of the ammoxidation of toluene,[1] and are tabulated in Table 2.

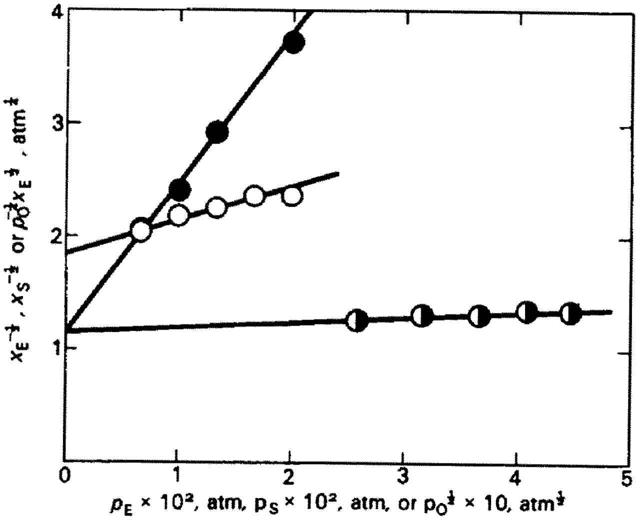


FIG. 5 Calculation of K_E, K_O, K_S, $k_E^0RT_0$ and $k_S^0RT_0$ in the ammoxidations of ethylbenzene and styrene at 400°.

○, p_{EO} vs. $x_E^{-\frac{1}{2}}$; ●, p_{SO} vs. $x_S^{-\frac{1}{2}}$; ◑, $p_O^{\frac{1}{2}}$ vs. $p_O^{\frac{1}{2}}x_E^{-\frac{1}{2}}$

TABLE 2. KINETIC PARAMETERS IN THE AMMOXIDATIONS OF TOLUENE, ETHYLBENZENE AND STYRENE AT 400°

Parameter \ Substrate		$PhCH_3$[a]	$PhCH_2CH_3$	$PhCH{=}CH_2$
K_{Sub}	(atm^{-1})	29·0	19·2	136
K_O	(atm^{-1})	0·15	0·25	—
$k_{Sub}^0RT_0$	(atm hr^{-1})	$6{\cdot}2 \times 10^2$	$8{\cdot}7 \times 10^2$	$1{\cdot}5 \times 10^2$
E_a	(kcal/mole)[b]	23	23	35
Order in p_O		0·45	0·39	0·50
Order in p_{Sub}		0·45	0·73	−0·10
x_{Sub}[c]		0·138[d]	0·206[d]	0·116[e]

[a] Cited from Ref. 1.

[b] Apparent energy of activation on the basis of the substrate consumption.

[c] With the standard composition of reactant gases.

[d] With catalyst volume of 2·5 ml and space velocity of 7200 hr^{-1}.

[e] With catalyst volume of 5·0 ml and space velocity of 3600 hr^{-1}.

The retardation effect of added styrene was interpreted by using the above values. Since the rate of styrene consumption is smaller than that of ethylbenzene, and the change of p_S during the reaction is negligible, Eqs 2, 5, 7 and 8 give approximation of v_E:

$$v_E \simeq \frac{p_{E0}x_E}{RT_0\left(\frac{V}{F}\right)} \simeq k_E^0 \frac{K_E p_{E0}\sqrt{(K_O p_O)}}{\{1 + K_E p_{E0} + K_S p_{S0} + \sqrt{(K_O p_O)}\}^2} \tag{12}$$

Here, p_{S0} is the partial pressure of added styrene. Hence, x_E can be calculated by using the above values of $k_E^0 RT_0$, K_E, K_S and K_O. Values of $x_{E\,calc.}$ agreed with those of $x_{E\,obs.}$, as shown in Fig. 3.

The rate of ethylbenzene consumption, the formations of styrene and benzonitrile in ammoxidation of ethylbenzene can be calculated assuming the consecutive reaction in terms of the above values of $k_E^0 RT_0$, $k_S^0 RT_0$, K_E, K_S and K_O. Since other carbon-containing products besides benzonitrile, styrene and hydrogen cyanide were trace amounts of carbon dioxide, benzene and toluene, the rate of formation of benzonitrile may nearly be equal to $v'_{N\,calc.}$, and that of styrene to $v'_{S\,calc.}$, as shown below:

$$v_{E\,calc.} \simeq \frac{p_{E0}x_E}{RT_0\left(\frac{V}{F}\right)} \simeq \frac{k_E^0 K_E p_{E0}\sqrt{K_O p_O}}{\{1 + K_E p_{E0} + \sqrt{(K_O p_O)}\}^2} \tag{10'}$$

$$v'_{N\,calc.} \simeq \frac{p_{E0}y_N}{RT_0\left(\frac{V}{F}\right)} \simeq x_E p_{E0} \frac{k_S^0 K_S \sqrt{K_O p_O}}{\{1 + K_E p_{E0} + \sqrt{(K_O p_O)}\}^2} \tag{13}$$

$$v'_{S\,calc.} \simeq v_{E\,calc.} - v'_{N\,calc.} \simeq \frac{p_{E0}y_S}{RT_0\left(\frac{V}{F}\right)} \tag{14}$$

The calculated rates are almost equal to the observed. Also, reaction orders of these rates can be obtained by plots of log ($v_{E\,calc.}$, $v'_{N\,calc.}$ or $v'_{S\,calc.}$) vs. log (p_{E0} or p_O). The calculated reaction orders are nearly in agreement with the observed as shown in Table 3.

TABLE 3. THE CALCULATED AND OBSERVED REACTION ORDERS IN THE AMMOXIDATION OF ETHYLBENZENE AT 400°

		Ethylbenzene consumption	Styrene formation	Benzonitrile formation
Order in p_O	calculated	0·41	0·28	0·90
	observed	0·39	0·25	0·90
Order in p_E	calculated	0·70	0·76	0·5–0·3
	observed	0·73	0·78	0·55

DISCUSSION

The fact that the reaction orders in hydrocarbon is smaller than unity (0·45th in toluene,[1] 0·73th in ethylbenzene and −0·10th in styrene) suggests the adsorption of the hydrocarbons on the catalyst surface. Since ethylbenzene reacts ca. 4 times as fast as styrene under similar conditions, the retarding effect of styrene is not due to the decrease of the concentration of the adsorbed oxygen on catalyst surface by the selective reaction of styrene with adsorbed oxygen, but to the competitive adsorption of styrene with ethylbenzene. Similar interpretation of the adsorption of aliphatic hydrocarbons on catalyst surface has been given in the oxidation of olefins over nickel oxide.[8] The retarding effect of styrene suggests that the adsorption of styrene is stronger than that of ethylbenzene. In fact, the adsorption equilibrium constant of styrene, obtained in terms of Langmuir–Hinshelwood mechanism, ($K_S = 136$ atm^{-1}) is larger than that of ethylbenzene($K_E = 19{\cdot}2$ atm^{-1}).

Although ammonia was not decomposed in the absence of oxygen, it was almost completely (98 %) decomposed in the presence of oxygen. But the decomposition was suppressed in the presence of aromatic hydrocarbons. The consumption of ammonia in ammoxidations of toluene and ethylbenzene was comparable to the nitrile formation. This suppression indicates that the adsorption of ammonia is weaker than that of aromatic hydrocarbons. In our previous paper,[1] the ammoxidation and ammonolysis of benzaldehyde suggests that ammonia was adsorbed on the site other than the site for substrates. Since rates of ammoxidation of aromatic hydrocarbons depend on the partial pressures of the hydrocarbon and oxygen but not on that of ammonia, ammonia is not involved in the rate-determining step for the ammoxidation. These results may exclude the mechanism for the nitrile formation via the reaction between aldehydes and (=NH).[9] Hence, the rate-determining step for the ammoxidation may be the oxidation of substrate.

The reaction orders in oxygen in ammoxidation of aromatic hydrocarbons were 0·45 in toluene,[1] 0·39 in ethylbenzene and 0·50 in styrene. In the oxidation of aliphatic hydrocarbons over Cr_2O_3,[10, 11] the reaction orders in oxygen were 0·47 for isobutene, 0·32 for propylene, 0·30 for ethylene and 0·17 for propane. This difference of orders suggests that oxygen and hydrocarbon are adsorbed on analogous adsorption sites and they are in a rapid equilibrium with the gases adsorbed on the catalyst surface. Since the reaction orders in oxygen were below 0·5 and the adsorption of oxygen over Cr_2O_3 was found to be predominant as O^- above 300°,[12] the reaction between adsorbed hydrocarbon and adsorbed oxygen in a dissociated form may participate in the rate-determining step. It was found that adsorbed oxygen acts as an electron-acceptor and adsorbed hydrocarbons act as electron-donors[13] Therefore, the mechanism for the oxidation may be expressed as:

$$\mathrm{Hc\,(gas)} \overset{K_{Hc}}{\rightleftharpoons} \mathrm{Hc^+\,(ads)} \tag{15}$$

$$\mathrm{O_2\,(gas)} \overset{K_O}{\rightleftharpoons} \mathrm{2O^-(ads)} \tag{16}$$

$$\mathrm{Hc^+\,(ads) + O^-(ads)} \underset{k_{-17}}{\overset{k_{17}}{\rightleftharpoons}} \mathrm{[Hc^+\,(ads)\,O^-\,(ads)]} \tag{17}$$

$$\mathrm{[Hc^+\,(ads)\,O^-\,(ads)]} \xrightarrow{k_{18}} \text{Intermediates or Products} \tag{18}$$

where Hc means hydrocarbon and (ads) means adsorbed gas on the catalyst.

Applying the Langmuir adsorption isotherms for a mixture gases to Eqs 15–18, the rate of hydrocarbon, v_{Hc}, is expressed as follows:

$$v_{Hc} = k^0_{Hc}\theta_{Hc}\theta_O \tag{19}$$

$$= k^0_{Hc}\frac{K_{Hc}p_{Hc}\sqrt{K_Op_O}}{\{1 + K_{Hc}p_{Hc} + \sqrt{(K_Op_O)} + \sum_i K_ip_i\}^2} \tag{20}$$

$$\simeq k_{Hc}(p_{Hc})^m(p_O)^n \tag{21}$$

where $k^0_{Hc} = k_{17}k_{18}/(k_{-17} + k_{18})$ and i means any miscellaneous compound.

Eq 20 suggests that (i) the stronger adsorption of hydrocarbon corresponds to the lower reaction order in hydrocarbon (m) and the higher reaction order in oxygen (n) and also that (ii) the stronger adsorption of additives correspond to the larger retardation of rate. This is the case for the ammoxidation of aromatic hydrocarbons. Similar suggestion has appeared in the oxidation of aliphatic hydrocarbons over Fe_2O_3.[11]

As mentioned above, a main pathway may be the consecutive reaction for the ammoxidation of ethylbenzene:

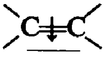
$$PhCH_2CH_3 \rightarrow PhCH{=}CH_2 \rightarrow PhCN + HCN \tag{22}$$

In the ammoxidation of styrene, partially oxidized products, i.e. benzaldehyde and formaldehyde, may be formed as intermediates by Eqs 15–18 and they react rapidly with adsorbed ammonia to form nitriles similarly as in the ammoxidation of toluene.[1] Hence, the main pathway for ammoxidation of ethylbenzene may be

$$PhCH_2CH_3 \xrightarrow[\text{slow}]{O} PhCH{=}CH_2 \xrightarrow[\text{slowest}]{O} (PhCHO + HCHO) \xrightarrow[\text{fast}]{NH_3, O} PhCN + HCN \tag{23}$$

The similarity of mechanistic feature between ammoxidations of ethylbenzene and of toluene implies that styrene formation from ethylbenzene is not simple dehydrogenation, but oxidative dehydrogenation.

The compositions of chromium catalysts are 42 % Cr^{5+} and 19 % Cr^{6+} in the fresh catalyst, 3 % Cr^{5+} and no Cr^{6+} in the used catalyst in ammoxidation of toluene, and 13 % Cr^{5+} and 0·4 % Cr^{6+} in the catalyst used and then treated with oxygen. It is apparent that the valence of Cr^{6+} is reduced rapidly by ammonia. Ethylbenzene gives a very little amount of styrene in the absence of oxygen. Therefore, unlike the dehydrogenation of cyclohexane,[14] the oxidation may be due to Cr^{5+}, but not to Cr^{3+}.

Apparent energies of activation for ammoxidation of alkylbenzenes (23 kcal/mole)[1] and oxidation of propane (22 kcal/mole)[11] were different from those for ammoxidation of styrene (35 kcal/mole) and oxidation of olefins (28–31 kcal/mole)[10, 11] over chromium oxide. The C—H bonds were oxidized in ammoxidations of toluene and ethylbenzene to form benzonitrile and styrene, respectively, while the C=C bond in the side chain was oxidized in ammoxidation of styrene forming benzonitrile and hydrogen cyanide. Since $K_S \gg K_T > K_E$, styrene having a vinyl group may strongly interact with catalyst. In the oxidation of olefins to the completely oxidized products over various oxides,[11] the absorbed state of olefins was suggested to be an undissociated π-complex,  . In the oxidation of n-butenes to butadiene and in the oxidation of propylene to acrolein over bismuth molybdate, the reactions were first order in olefin and independent of oxygen and products and the abstraction of allylic hydrogen atom by an adsorbed oxygen atom was suggested as the rate-determining step.[5] This kinetic order implied that olefins were adsorbed very weakly on the catalyst and they were not adsorbed as an undissociated π-complex. Therefore, hydrocarbons, which may interact with catalysts by alkyl group, may partially be oxidized in their alkyl groups to form, for example, homologous aldehydes, alkenes, etc, having the same number of C atoms, while hydrocarbons, which strongly interact with catalysts by C═C bond, may be oxidized by breaking their C═C bonds.

EXPERIMENTAL

Materials. Guaranteed reagent grade ethylbenzene was purified by successive shaking with H_2SO_4, $NaHCO_3$ and water, followed by drying over Na and then distillation (b.p. 135·8–136·0°). Chemically pure grade styrene was employed (b.p. 145°). Benzonitrile was purified by distillation over P_2O_5 (b.p. 190°). Commercial ammonia, N_2 and O_2 were employed. The same catalyst as that in the previous work was used.[1]

Apparatus and procedures. The apparatus and procedure were similar to those employed in the previous paper.[1] But a combined column of 25 wt% paraffin wax on Chamelite CK 40 cm and 30 wt% PEG#6000 on Celite 545 10 cm, column I, was used for ethylbenzene, styrene and benzonitrile. HCN was absorbed in an alkali scrubber connected to the experimental apparatus and its amount was determined by the titration with $AgNO_3$ aq. Styrene and benzonitrile were identified by means of GLC and UV spectral analysis comparing with the corresponding authentic samples. Amounts of total Cr, Cr^{6+} and Cr^{5+} was determined by iodometry.[15]

Nomenclature. A, Ammonia; E, Ethylbenzene; O, Oxygen; S, Styrene; T, Toluene; Sub, Substrate; a, e, n, and s, Kinetic orders in A. E. O and S, respectively; p_A, p_O, p_{Sub}, Partial pressures of subscripted substance; Subscript 0 means initial stage of reaction; v_{Sub}, Rate of consumption of subscripted substance on ammoxidation, mole ml^{-1} hr^{-1}; v'_N, v'_S, Rate of formation of benzonitrile and styrene, respectively, mole ml^{-1} hr^{-1}; k_{Sub}, Rate constant for the reaction of substrate; $k^0{}_{Sub}$, Rate constant for the reaction of substrate on catalyst surface; x_{Sub}, Conversion of substrate, mole mole^{-1}; y_S, y_N, Yield of styrene and benzonitrile, respectively, mole mole^{-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}.

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