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Studies on the Ammoxidation of N-Heterocyclic Compounds. IV.[1) Vapor-Phase Ammoxidation of Lutidine Isomers

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The kinetics of heterogeneous vapor-phase ammoxidation of lutidine isomers was studied over a Cr_2O_3–Al_2O_3 catalyst in a flow system. The reaction was carried out at atmospheric pressure and at a temperature of 360°. 3-Cyano-5-methylpyridine, 4-cyano-3-methylpyridine, 2-cyano-6-methylpyridine, 2-cyano-5-methylpyridine and 2-cyano-3-methylpyridine were produced selectively at low conversion from 3,5-lutidine, 3,4-lutidine, 2,6-lutidine, 2,5-lutidine and 2,3-lutidine respectively. 2-Cyano-4-methylpyridine and 4-cyano-2-methylpyridine were produced in same amounts from 2,4-lutidine.

The reaction rate depended on the partial pressure of lutidine and oxygen. Experimental rate data were well interpreted by Langmuir-Hinshelwood mechanism, where the rate determining step was the surface reaction between adsorbed lutidine molecules and adsorbed oxygen molecules.

We have shown that cyanopyridines are produced selectively from picolines by ammoxidation over the noncrystallized cromium oxide catalyst supported on alumina, and its rate determining step is the surface reaction between competitively adsorbed picoline and oxygen on the active sites.[1)

The present paper reports studies on ammoxidation of lutidine isomers over the same catalyst.

Zvakova, *et al.*[3) have studied the reaction products of ammoxidation of lutidines over V_2O_5–Al_2O_3 catalyst. However, there have been few detailed reports for this reaction.[4)

In addition with the previous work for picolines, a detailed analysis of ammoxidation of lutidines should be necessary and interesting for attaining a general knowledge of ammoxidation of N-heterocyclic compounds.

Experimental

Materials——Lutidines were obtained from Koei Chem. Co., and purified by further distillation, and confirmed their purity by gas chromatograph. Oxygen, ammonia and nitrogen from cylinders were dried by passage through beds packed NaOH and sodalime. Alumina was obtained from Sumitomo Chem. Co. (KHD 8/10 mesh).

Catalyst——The catalyst employed in this study was γ-alumina containing 5% Cr_2O_3. This catalyst was prepared by an impregnation procedure, using aqueous solution of $(NH_4)_2Cr_2O_7$. After impregnation, the resulting material was dried for 3.5 hr at 150° and calcinated in air at 550° for 3 hr.

Procedure——The experiments were carried out in tubular flow reactor system, described in an earlier paper,[5) at atmospheric pressure. Our experimental conditions are shown in Table I. The reaction rate was measured at low conversion, and calculated by following equation.

$$r_S = \frac{p_{S0} x_S}{W/F} \qquad (1)$$

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1) Part III: J. Okada, S. Morita and Y. Miwa, *Yakugaku Zasshi*, **93**, 1364 (1973).

2) Location: *Yoshida-Shimoadachi-cho, Sakyo-ku, Kyoto.*

3) N. Kucharczyk and A. Zvakova, *Coll. Czechoslov. Chem. Commun.*, **28**, 55 (1963).

4) G. Mayurnik, A.F. Moshetto, H.S. Bloch and J.V. Scudi, *Ind. Eng. Chem.*, **44**, 1630 (1952); V.I. Trubinikov, E.S. Zhudanovich and N.A. Preobrazhenskii, *Khim. Farm. Zh.*, **3**, 42 (1969).

5) J. Okada, S. Morita and Y. Miwa, *Yakugaku Zasshi*, **92**, 1443 (1972).

where, r_S[atm·cm^3·g-cat^{-1}·min^{-1}] means the reaction rate of lutidine, p_{S0}[atm] means the inlet partial pressure of lutidine, x_S[—] means the conversion of lutidine, W[g] means the weight of catalyst, and F[cm^3·min^{-1}] means the total flow rate.

The partial pressure of lutidine in catalyst bed was assumed to be the average of inlet and outlet partial pressures, and that of oxygen or ammonia was assumed to be the inlet partial pressure.

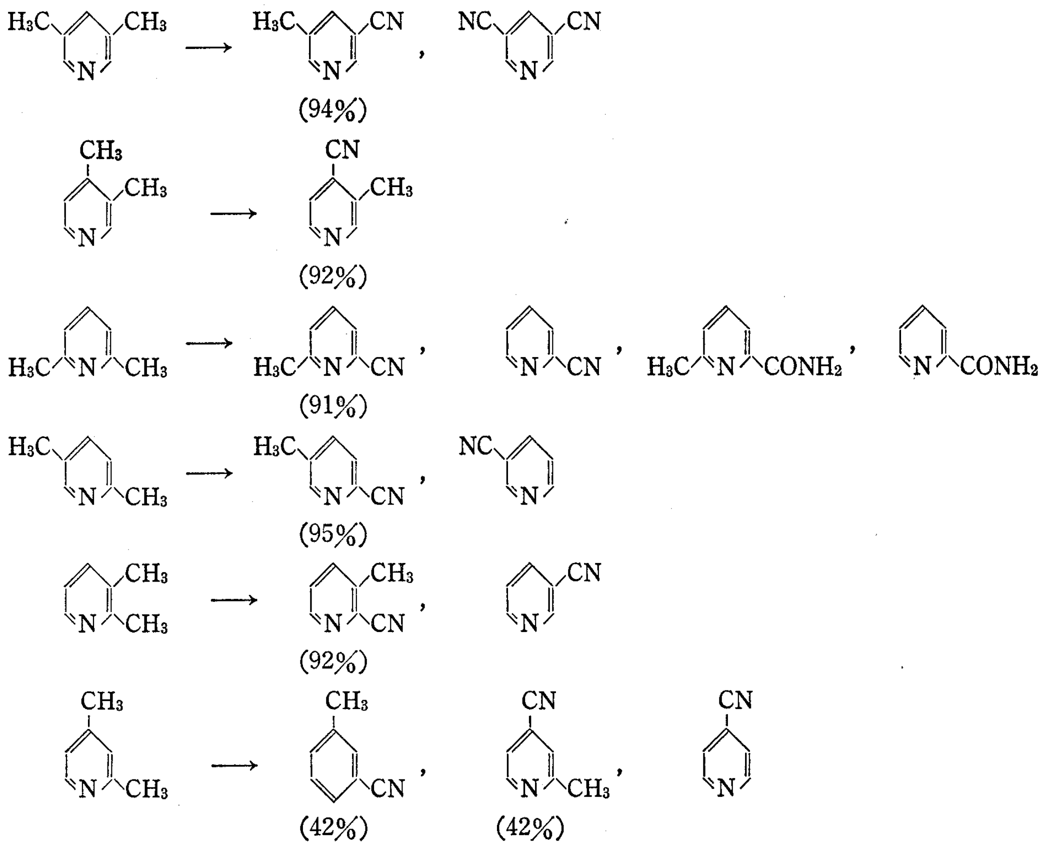
Table I. Experimental Conditions

Reaction temp.	360°
Total press.	1.0 [atm]
Lutidine press.	0.25—2.0×10^{-2} [atm]
Ammonia press.	8.0×10^{-2} [atm]
Oxygen press.	2.0—30.0×10^{-2} [atm]
Catalyst	1.0—4.0 [g]
Total flow rate	100—300 [cm^3·min^{-1}]

Identification of Products——The products of this reaction are shown in Chart 1. The starting materials, lutidines, were distilled and the residue was purified by silica gel chromatography with benzene–ethyl acetate and identified by mp, infrared spectrum (IR) and nuclear magnetic resonance (NMR).

Zvakova, *et al.*[3] have reported that 2-methyl-5-cyanopyridine was obtained from 2,5-lutidine, but the product obtained in this work was determined to be 2-cyano-5-methylpyridine, because in NMR spectra (100 MHz $CDCl_3$) the triplet at δ 2.43 ppm (3H, $J=0.6$ Hz) could be assigned to the methyl protons at the 5-position.

The selectivity of monocyanopyridine was more than 90% at conversion within 25%, except for 2,4-lutidine, and the amounts of CO_2 and CO were trace.



( ); selectivity at low lutidine convesion (*ca.* 20%)

Chart 1. Reaction Products of Ammoxidation

Analysis——Analysis of inlet and outlet gas was carried out by injecting 2 ml of sample into gas chromatograph connected to the reactor (Yanagimoto Co. GCG-550T). The used column was packed with 10% polyethylene glycol adipate on Neopack 1A (60/80 mesh) for lutidines and cyanopyridines analysis, with silica gel (80/100 mesh) for CO_2 analysis and with Molecular sieves 5A (80/100 mesh) for CO analysis.

Results and Discussions

In our experimental conditions, lutidines were not converted without oxygen. External and internal diffusion effects were negligible, which were checked in a similar manner as previous paper.[5]

The diffusion effects of ammonia and oxygen were also negligible, since oxidation of ammonia was negligible over 5% Cr_2O_3–Al_2O_3 catalyst at 360°, and the partial pressure of oxygen or ammonia was five times as much as that of lutidine in our conditions.

From these results, the rate determining step of lutidine ammoxidation, in our conditions, may be chemical reaction.

Chart 1 shows the products from lutidines by ammoxidation. The products other than monocyanopyridines were obtained in the higher catalytic activity conditions. After the catalyst was used about eight hours, monocyanopyridines were produced with the higher selectivity more than 90% at conversion within 25%.

From the position of nitrile group of the produced cyanopyridines, it is considered that methyl group at the 2-(6-) or 4-position is more reactive than methyl group at the 3-(5-) position. In the first reaction step, therefore, methyl group at the 2- or 4-position is oxidized and converted to nitrile. And in the case of 2,4-lutidine, same amounts of 2-cyano-4-methylpyridine and 4-cyano-2-methylpyridine are obtained, because methyl groups at the 2- and 4-position are oxidized at the similar reaction rate. By the easiness of oxidative decomposition of methyl group at the 2-position, 2-cyanopyridine from 2,6-lutidine, 3-cyanopyridine from 2,3-lutidine and 2,5-lutidine, 4-cyanopyridine from 2,4-lutidine, are obtained respectively as by-products.

In previous paper,[1] we have found that 4-picoline and 2-picoline react at the similar rate, but the rate of 3-picoline is about 1/10. This difference in reaction rates of picolines is interpreted by assuming that the hydrogen atom of methyl group at the 2- or 4-position can be removed more easily than hydrogen atom of methyl group at the 3-position by the electron-drawing effects of nitrogen in pyridine ring.

This reactivity of methyl groups is consistent with the above mentioned reactivity which is supposed from reaction products of lutidines. Then, it is considered that the ammoxidation of lutidine, as well as picoline, is controlled by the process in which the hydrogen atoms are removed from methyl group by the surface reaction between adsorbed lutidine and oxygen on the active site. The model shown by Equation (2)—(5) is assumed for lutidine ammoxidation.

$$\text{Py–CH}_3 + \alpha \overset{K_S}{\rightleftarrows} (\text{Py–CH}_3)_{ad} \tag{2}$$

$$\text{O}_2 + \alpha \overset{K_B}{\rightleftarrows} (\text{O}_2)_{ad} \tag{3}$$

$$(\text{Py–CH}_3)_{ad} + (\text{O}_2)_{ad} \xrightarrow{k_S} (\text{Py–CH}_2\cdot)_{ad} \tag{4}$$

$$(\text{Py–CH}_2\cdot)_{ad} \xrightarrow{\text{NH}_3,\ \text{O}_2} \longrightarrow \longrightarrow \text{Py–CN} \tag{5}$$

where, α means the active site and $(\ )_{ad}$ means the adsorbed molecule.

In previous paper,[1] the authors have reported that oxygen is adsorbed in a molecular state, in other words, not dissociated into an atomic state, when adsorbed on the active site at the temperatures under 380°. In this work, all experiments were carried out at 360°, then it is assumed for oxygen to be adsorbed in a molecular state (Equation (3)).

If the adsorption processes (Equations (2) and (3)) are in an equilibrium state, and the rate determining step is the surface reaction (Equation (4)), the reaction rate of lutidine, r_S, is given by Equation (6):

$$r_S = \frac{k_S K_S p_S K_B p_B}{(1+K_S p_S + K_B p_B)^2} \tag{6}$$

where, p_S or p_B [atm] means the partial pressure of lutidine or oxygen, k_S [atm·cm^3·g-cat^{-1}·min^{-1}] means the rate constant of surface reaction, K_S or K_B [atm^{-1}] means the adsorption equilibrium constant of lutidine or oxygen.

Equation (6) is transformed as follows:

$$\sqrt{\frac{p_S}{r_S}} = \sqrt{\frac{K_S}{k_S K_B p_B}}\, p_S + \frac{1+K_B p_B}{\sqrt{k_S K_S K_B p_B}} \tag{7}$$

$$\sqrt{\frac{p_B}{r_S}} = \sqrt{\frac{K_B}{k_S K_S p_S}}\, p_B + \frac{1+K_S p_S}{\sqrt{k_S K_S K_B p_S}} \tag{8}$$

Therefore, the relationship between $\sqrt{p_B/r_S}$ and p_S should be linear from Equation (7), when p_B is constant, and the relationship between $\sqrt{p_S/r_S}$ and p_B should be also linear from Equation (8), when p_S is constant.

The logalithmic plots of r_S *vs.* p_S and r_S *vs.* p_B are shown in Fig. 1 for the experimental data of 3,5-lutidine. The relationships of r_S *vs.* p_S at constant p_B (8.0×10^{-2} [atm]) are shown with closed circles and the relationships of r_S *vs.* p_B are shown with vacant circles, when the the inlet partial pressure of lutidine, p_{S0}, is constant (0.5×10^{-2} [atm]). And $\bar{p}_S$ indicates the average of four measurements shown with vacant circles. In these cases, experiments were carried out at constant partial pressure of ammonia ($p_A=8.0\times10^{-2}$ [atm]). In an earlier paper,[1] we have found that the rate of ammoxidation is not affected by ammonia pressure. Then, in this work the effects of ammonia were not checked.

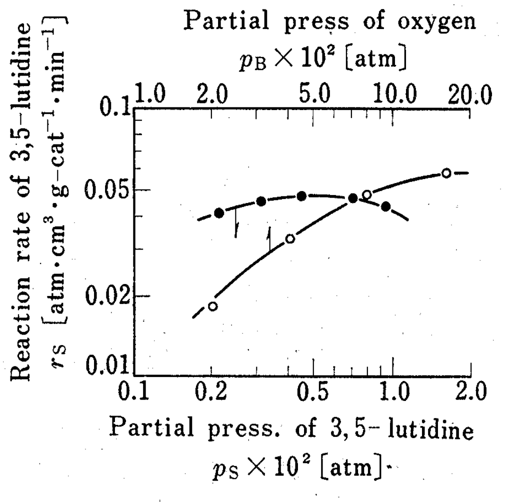


Fig. 1. Ammoxidation of 3,5-Lutidine conditions; reaction temp. 360°

$W/F=1.0\times10^{-2}$[g-cat·min·ml^{-1}]
ammonia ($p_A=8.0\times10^{-2}$[atm])
—●—: $p_B=8.0\times10^{-2}$[atm]
—○—: $\bar{p}_S=0.462\times10^{-2}$[atm]

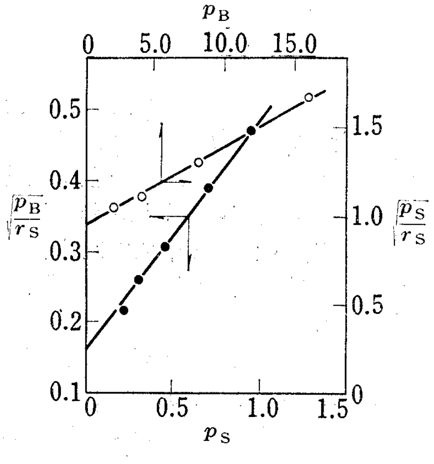


Fig. 2. Linearization Plots for Ammoxidn. of 3,5-Lutidine

The plots of $\sqrt{p_S/r_S}$ *vs.* p_S and $\sqrt{p_B/r_S}$ *vs.* p_B for the data of Fig. 1 are summarized in Fig. 2. The linearity existing in these plots shows the validity of the rate expression, Equation (6). The values of k_S, K_S and K_B were estimated by nonlinear least square method,[6,7] in which the initial parameters were determined by using the values calculated from the linearization plots, Fig. 2. In Fig. 1, the curves are drawn by using these estimated values, and they agree with the experimental data.

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[6] J.R. Kittrell, R. Mezaki and C.C. Watson, *Ind. Eng. Chem.*, **57**, 18 (1965).
[7] All calculations were carried out in Data Processing Center, Kyoto University.

Table II. Nonlinear Least Square Estimate of Parameter Values[a] and 95% Confidence Limits

substrate	k_S [atm·cm^3/g-cat·min]	K_S [1/atm]	K_B [1/atm]
3,5-lutidine	0.351±0.030	451 ± 75.3	15.1 ±2.91
3,4-lutidine	4.89 ±1.24	96.9± 23.4	6.01±2.00
2,6-lutidine	1.66 ±0.301	139 ± 30.8	9.30±2.64
2,5-lutidine	1.87 ±0.504	109 ± 40.9	7.16±2.33
4-picoline	4.40 ±0.854	79.4± 15.6	7.60±2.17
2-piooline[b]	2.72	137	12.2
3-picoline	0.168±0.085	504 ±269	14.9 ±9.15

a) values at 360° b) calculated from Arrhenius equations[1]

The ammoxidation of 3,4-lutidine, 2,6-lutidine and 2,5-lutidine were studied in the same manner. The optimum parameter values and the 95% confidence limits by nonlinear least square method are shown in Table II. The values for picolines reported in our previous paper[1] are shown together in this table. The values of K_B must be equal for the all substrates, but these estimated values for each substrate are somewhat different.

In the ammoxidation system, lutidines are decomposed to by-products simultaneously by the side-reaction other than the main reaction producing cyanopyridines. Because the selectivity of monocyanopyridines was more than 90% at low conversion, we calculated the ammoxidation rate by the rate of change of picoline or lutidine. Then the observed reaction rate contains this side-reaction rate. The convergent values of K_B, thus, may be somewhat different because of the difference of these side-reaction rate.

Conclusion

From these kinetic analysis, we conclude that the ammoxidation of methylpyridines over the 5% Cr_2O_3–Al_2O_3 catalyst is controlled by the surface reaction between adsorbed methylpyridine molecules and adsorbed oxygen molecules. And the reactivity of methyl group at the 2-(6-) or 4-position is higher than that of methyl group at the 3-(5-) position. In the cases of 3,4-lutidine, 2,3-lutidine and 2,5-lutidine, therefore, only the methyl group at the 2- or 4-position is oxidized at first and monocyanopyridine is produced in the first step of ammoxidation.

The correlation between the reaction rate and the substrate structure appears to be an interesting problem. However, this problem could not be studied in detail, because the degree of catalyst decay was different for each substrate. The reaction rates should be compared at constant activity conditions by the pulse method or the competitive method. The conditions obtaining industrially important dicyanopyridines will be the subject to study in future.

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