CATALYTIC VAPOR PHASE OXIDATION OF MONOMETHYLPYRIDINES TO PYRIDINECARBOXYLIC ACIDS

S. K. BHATTACHARYYA, VIJAY SHANKAR, AND A. K. KAR

Department of Applied Chemistry, Indian Institute of Technology, Kharagpur, India

The three picoline isomers were subjected to catalytic vapor phase oxidation over a series of vanadium catalysts in fixed and fluidized beds. 2-Picoline on oxidation yielded pyridine -2-aldehyde and 2-pyridoin. 3-Picoline produced traces of nicotinaldehyde, nicotinic acid, and CO₂. 4-Picoline or γ -picoline yielded isonicotinaldehyde (I), two isomers of 1,2-di(4-pyridyI)-1,2-ethanediol (II), and isonicotinic acid (III). 4-Picoline gave on oxidation over a V₂O₅-kieselguhr catalyst, traces of I, 12.6% of II, 71.6% of III, and 4.7% CO₂ (temperature 350° C., air rate 50 ± 2 liters per hour at 30° C., picoline feed rate 1.1 to 1.3 grams per hour, steam feed rate 29 to 31 moles per mole of 4-picoline). Fluidization of the catalyst did not improve the results. A mechanism has been suggested for the oxidation of 4-picoline.

The pyridinecarboxylic acids, particularly nicotinic and isonicotinic acids, are very important as precursors of a number of potential drugs.

Monomethylpyridines, commonly called picolines, which are obtainable as by-products from the coal tar distillation industry and also synthetically, can form important starting materials for the manufacture of these acids. The commercial method involves the liquid phase oxidation of the picolines, using sulfuric acid (in the presence of selenium as a catalyst), and potassium permanganate or nitric acid as an oxidizing agent. Attempts have also been made to oxidize the picolines in the vapor phase using air as oxidizing agent (3-8, 10, 11, 13, 15). But information on the nature of the catalysts used and other operational details has not yet been published and is carefully guarded by patents. The authors have carried out the reaction over fixed as well as fluidized beds of a number of catalyst compositions over a wide range of operating variables such as temperature, picoline feed rate, air-picoline ratio, and catalyst composition. The reaction does not follow the normal course of oxidation and a number of interesting side reactions have been discovered. The products have also been isolated and a possible mechanism for the formation of the various products has been suggested.

Experimental Procedure and Arrangement

A flow diagram of the apparatus used is shown in Figure 1. The apparatus is comprised of three main units: the feeding system for introducing controlled amounts of picoline, air, and steam; the reactor; and the product recovery unit.

Feeding System. Dry and purified air passing through the mercury safety device, S, was divided into two streams, one passing through flowmeter F_1 into the picoline bubbler surrounded by a constant temperature water bath, WB, and the other (secondary air) through flowmeter F_2 into the reactor after being mixed with the vaporized picoline.

Whenever water vapor was fed with the reaction mixture the secondary air was led through a water bubbler, kept in a constant temperature glycerol bath, GB. The entire tube length between the bubblers and the reactor was maintained at 60° C. by Kanthal wire to prevent the condensation of the vapors. A manometer, M, recorded the static pressure in the system.

Reactor. The reactor (Figure 2) was made of borosilicate

glass tubing 1 inch in internal diameter and 7 inches long. Another glass tube of 0.3-inch bore, sealed at one end and kept concentric with the reactor tube by means of a separable standard ground-glass joint, was used for inserting the thermocouple. The reactor consisted of two sections: the preheater zone filled with broken glass and the catalyst zone where the catalyst was packed between two plugs of purified asbestos wool. The two zones were heated by two separate tubular heaters controlled by variable transformers.

During the reaction, the temperature of the catalyst bed was maintained constant by regulating the heat input. The temperature of the incoming reaction mixture was kept constant by keeping the temperature of the preheater zone unchanged. Since the temperature of the preheater zone was always higher than that of the catalyst zone, the glass packing was extended about an inch into the catalyst zone, so that the catalyst temperature was not influenced to any appreciable degree by the temperature of the preheater. The temperature of the catalyst was thus kept uniform throughout.

Product Recovery. The reaction products, which were always associated with a large excess of air, were passed successively through air-, water-, and ice-cooled condensers. The gases were then bubbled through water, and finally through a standard (5%) solution of potassium hydroxide in order to absorb the carbon dioxide produced in the reaction. The residual gases were passed through a gas meter, GM.

Materials Used

Chemicals. Chemically pure grade chemicals were used in the preparation of all the catalysts studied in the present work. The picolines were carefully fractionated and further purified by the methods recommended by Vogel (14). 4-Picoline was purified by the method of Kollof and Hunter (9).

Preparation of Catalysts. The chief component of all the catalysts studied in the present investigation was vanadium pentoxide. Ammonium vanadate was dissolved in a solution of an equal weight of oxalic acid and impregnated on the carrier. On drying and heating in a current of air, the oxalate decomposed, leaving behind supported vanadium pentoxide. Promoted catalysts were prepared by mixing a calculated quantity of an aqueous solution of a salt (generally nitrate) of the promoting metal with the solution of ammonium vanadate in oxalic acid, and impregnating this homogeneous solution on a carrier. On heating, the salts decomposed, leaving the metallic oxide behind.

The prepared catalysts were between 0.12 and 0.17 cm. in size and 20-cc. volume was used in each case. All the catalysts, when freshly prepared, were treated with an air-picoline mixture for a minimum of 4 hours before the start of the experimental runs, for stabilizing the catalytic activity level,





the conditions of treatment being established by preliminary experimentation.

Identification and Analysis of Products

From 4-Picoline. The products obtained by passing a mixture of air and 4-picoline vapors over a typical oxidation catalyst were qualitatively analyzed. The products, as expected, contained a carbonyl compound which was confirmed to be pyridine-4-aldehyde (melting point of the 2,4-dinitrophenyl hydrazone was 275° C.). The product on

neutralization with alkali and concentration deposited two crops of crystals, octahedral crystals [m.p. 210° C. (I)] and needle-shaped crystals [m.p. 175° C. (II)]. Unreacted picoline was obtained by distilling the alkaline solution, treating the distillate with an excess of caustic soda, and extracting with ethyl ether. The picrate showed a melting point of 164–65° C.

The residue left after distilling off the water and picoline consisted of the sodium salt of isonicotinic acid and an unidentified dark brown compound. The acid was liberated



Figure 3. Infrared spectra of trans isomer of 1,2-di(4-pyridyl)-1,2-ethanediol



Figure 4. Infrared spectra of cis isomer of 1,2-di(4-pyridyl)-1,2-ethanediol

by dissolving the residue in water and acidifying to pH 3.6 by adding hydrochloric acid. The precipitated acid on purification showed a melting point of 317° C. in a sealed tube. The presence of isonicotinic acid was also confirmed by paper chromatography. The presence of a single spot on the chromatogram also showed that no other acid was formed in the reaction.

COMPOUNDS I AND II. Mathes and Souermilch (12) in an attempt to get 4-pyridoin by the benzoin condensation of pyridine-4-aldehyde in the presence of potassium cyanide obtained two isomers of 1,2-di(4-pyridyl)-1,2-ethanediol. Compounds I and II resembled these compounds in physical properties. It was concluded that some such products might be formed during the vapor phase oxidation of 4-picoline. The constitution of these compounds was therefore established by the following experiments.

Microanalysis showed the following results:

	C	H	N
Calculated, %	66.65	5.59	12.96
Found, % Comp. I Comp. II	65.15 65.83	5.79 5.92	12.95 12.29

Since these compounds contain hydroxyl groups attached to contiguous carbon atoms $(N \bigcirc CH(OH) . CH(OH) .$ $(N \bigcirc CH(OH) .$ $(N \bigcirc CH(OH) . CH(OH) .$ $(N \bigcirc CH(OH) . CH(OH) .$ $(N \bigcirc CH(OH) .$

the aldehyde:

N CH(OH). CH(OH) N + KIO₄ =
$$2N$$
 CHO + KIO₃ + H₂O

Pyridine-4-aldehyde could actually be identified in the product obtained from such reactions. The yield was quantitative. When oxygen absorbed by these compounds from periodate ion was estimated, the above structure was confirmed. Further confirmation was obtained by studying the infrared spectra. The spectra for both the isomers in the Nujol phase (Figures 3 and 4) exhibit characteristic strong OH stretching frequencies in the regions 2800 to 3300 cm.⁻¹ and 2800 and 2900 cm.⁻¹ for trans and cis isomers, respectively, and indicate strong intermolecular hydrogen bondings. The characteristic C==C and C==N absorptions for pyridine in the 1600- to 1500-cm.⁻¹ region are also indicated.

ESTIMATION OF PRODUCTS. Pyridine-4-aldehyde was estimated gravimetrically by precipitating the 2,4-dinitrophenyl hydrazone. Isonicotinic acid could be conveniently estimated by titrating against standard alkali. The glycols were estimated together by oxygen absorption from the periodate titration. For the estimation of 4-picoline the base was steamdistilled from the products in the presence of excess of sodium hydroxide. The distillate was titrated with standard hydrochloric acid, using a few drops of a mixed indicator consisting of dimethyl yellow and methylene blue in alcohol. The change of color from green to blue violet between pH 3.4 and 3.2 was sharp. Carbon dioxide was estimated by scrubbing the gases emerging from the reactor (after recovery of solid and liquid products) with a standard solution of potassium hydroxide and estimating the residual hydroxide volumetrically.

From 3-Picoline. In this case the products of oxidation over vanadium pentoxide supported on kieselguhr were only traces of nicotinaldehyde, nicotinic acid, unconverted 3-picoline, and carbon dioxide. A dark brown substance was also formed at higher temperatures, but could not be isolated and identified.

From 2-Picoline. The products from the oxidation of 2-picoline over V_2O_5 -pumice (51.84 to 100) consisted of a dark brown solid and a greenish blue substance which turned brown on exposure to air. A qualitative examination of the products

						\bigwedge
showed	the	presence	of 2-pyridoin		-CH(OH)CO-	
				N		N

and pyridine-2-aldehyde. No significant conversion to picolinic acid was obtained. The analysis of the products from a typical run carried out at 300° C. with a molal air to 2picoline ratio of 80 and a space velocity of 2400 to 2500 liters per hour per liter over a catalyst containing V_2O_{δ} on kieselguhr in the ratio of 51.84 to 100 gave:

Moles of steam fed/mole of 2-picoline	15
Conversion, %	1 05
To CO ₂	1.1
To 2-pyridoin	14.5 (estimated by HIO4 oxidation)
Total bases in product, $\%$	$\frac{78.1}{95.65}$

Results and Discussion

Oxidation of 4-Picoline. The oxidation of 4-picoline was studied over numerous catalysts, V_2O_5 being the chief catalytic component. The influence of different operating conditions such as supports, promoters, temperatures, space velocity, and air-picoline ratio was studied exhaustively and the results under best conditions are presented in Table I.

In general, the catalysts were active above 350° C. With increasing temperatures the conversion to isonicotinic acid increased, reached a maximum, and then decreased because of

greater conversion to carbon dioxide. Change in the molar concentration of the reactants showed little effect on the conversion to isonicotinic acid. With increase in the space velocity the conversion to isonicotinic acid declined slightly. Maximum conversion was obtained with V_2O_5 supported on kieselguhr (V_2O_5 -kieselguhr, 51.83 to 100). The conversion to isonicotinic acid was 52.5% at 360° C. with a molal airpicoline ratio of 178.2 and a space velocity of 2435 liters per hour per liter of the catalyst.

EFFECT OF FEEDING STEAM WITH REACTION MIXTURE. The presence of 1,2-di(4-pyridyl)-1,2-ethanediol in the oxidation products of 4-picoline indicated the existence of a side reaction competing with the main reaction—i.e., oxidation of 4-picoline to isonicotinic acid. The fact that the diol is formed by the condensation of pyridine-4-aldehyde can be assumed without any doubt, since the compound was isolated by Mathes *et al.* (11) by the benzoin condensation of the aldehyde. The formation of this compound during the benzoin condensation can be explained by the following mechanism:



While this explanation might hold good for the benzoin condensation of the aldehyde in the liquid phase, the vapor phase processes can offer an alternative route for the formation of the diol. The methyl groups attached at the 2- and 4positions of the pyridine ring are very active. This leads to a special type of condensation of 2- and 4-picolines with carbonyl compounds, depending upon conditions. Thus, benzaldehyde condenses with 4-picoline to give 4-stilbazole:

$$N \longrightarrow CH_{3} + C_{6}H_{5}CHO \longrightarrow N \longrightarrow CH_{2}-CH(OH) \longrightarrow C_{6}H_{5} \xrightarrow{-H_{2}O} N \longrightarrow CH=CH-C_{6}H_{5}$$

$$4-Stilbazole$$

The intermediate compound is formed by heating in water and later, on dehydration with acetic anhydride, it is converted to the stilbazole.

Since pyridine-4-aldehyde is an intermediate product in the oxidation of 4-picoline to isonicotinic acid, its possible condensation with the unreacted 4-picoline offers a new explanation for the formation of the diol according to the following steps:

$$R.CH_{3} + OHCR \longrightarrow$$

$$RCH_{2} - CH(OH)R \xrightarrow{-H_{2}O} RCH = CHR$$

$$I \qquad II \downarrow O$$

$$RCH - CHR \xleftarrow{H_{2}O} RCH - CHR$$

$$\downarrow \qquad OH OH OH$$

$$IV \qquad III$$

$$R = (- N)$$

From the products of 4-picoline oxidation, only IV could be isolated in pure form. Compounds I, II, and III were present in too small quantities in the reaction products and hence could not be isolated in pure form. The dehydration of compound I in step 2 suggested that the presence of large amounts

Table I. Comparative Efficiency of Catalysts in Oxidation of 4-Picoline

	Optimum Conditions					
Catalysts		Space velocity,	Molal	% Conver		
	<i>Temp.</i> , ° Ĉ.	liters/ hr./liter	Ratio Air/Picoline	Isonicotinic acid	Carbon dioxide	S.T.Y., G./Hr./Literª
V_2O_5 -pumice, 51.84 to 100	340 <i>°</i>	2395	231.3	41.4	2.4	23.5
V_2O_5 -kieselguhr, 51,84 to 100	340	2414	173.6	50.9		38.8
V_2O_3 -kieselguhr, 70 to 100	320	2414	180.0	47.33	3.0	34.8
V_2O_5 -kieselguhr, 31.1 to 100	320	2442	163.0	41.36		33.93
V_2O_5 (unsupported)	320	2439	152.0	44.30	7.95	39.95
V ₂ O ₅ -CoO-kieselguhr, 31,1:1,288:100	360	2431	174.0	44.31	4 85	33 90
$V_{2}O_{3}$ -MoO ₃ -kieselguhr, 31,09:2,739:						00.70
100	340	2486	166.1	44 9	2 58	36.9
$V_{2}O_{3}$ -Cr ₂ O ₃ -kieselphur, 51,84:5,18:			10011		2.00	50.7
100	340	2375	159 0	48 78	5 77	30 05
$V_{\circ}O_{\circ}$ -Fe $_{\circ}O_{\circ}$ -kieselguhr, 51, 84:5, 18:100	320	2414	154 0	48 94	7 95	42 06
V_2O_5 (fused)	440	2138	153.0	36.36	2.80	27.90
^a S. T. Y. = Space time yield						

^b Temperature at which % activity to acid was maximum.

of steam in the reaction mixture might be helpful in checking the subsequent reactions, since dehydration would be difficult in the presence of steam.

Encouraging results were obtained when steam was passed along with the reaction mixture. The conversion to acid rose as high as 66.2% compared with 51% without the use of steam. The data obtained with three catalysts are given in Table II. Use of about 30 moles of steam per mole of 4picoline was optimum.

A complete analysis of the reaction products (Table III) revealed that the increase in the conversion of 4-picoline to isonicotinic acid was accompanied by an equivalent drop in conversion to the diol. This observation establishes the fact that a check on the dehydration step suppressed the side reaction to the diol.

Another possible cause for the increased conversion to isonicotinic acid may be the oxidation of the diol itself, which is helped by the presence of steam:

$$\begin{array}{cccc} \text{RCH-CHR} & \stackrel{O}{\longrightarrow} & \text{R-CO-CO-R} & \stackrel{O+H_{1}O}{\longrightarrow} & 2 & \text{RCOOH} \\ & & & & \\ & &$$

4-Pyridil

The over-all picture of the reaction can thus be represented as:



Table II. Effect of Feeding Steam with Reaction Mixture in Oxidation of 4-Picoline

Space velocity = 2450 ± 50 liters/hr./liter Molal ratio, air/4-picoline = 165 ± 10 Catalyst volume = 20 cc.

Temp., ° Ĉ.	Moles Steam/Mole 4-Picoline	% Conversion to Isonicotinic Acid
Cata	lyst. V_2O_5 -Kieselguhr, 52	1.84 to 100
340	0.0 7.0 11.5 20.6 29.4 43.5	50.9 55.1 55.2 64.7 66.2 65.4
Catalyst. 320	V ₂ O ₅ -Cr ₂ O ₃ -Kieselguhr, 0.0 22.0	51.84:5.18:100 45.40 66.09
Catalyst. 320	V ₂ O ₅ -Fe ₂ O ₃ -Kieselguhr, 0.0 16.0	51.84:5.18:100 48.94 65.50

The presence of steam in the reaction mixture can be said to be helpful in two ways—suppressing the dehydration step and thus suppressing in turn the condensation of the aldehyde with unreacted 4-picoline, and promoting the direct oxidation

of the condensation products to isonicotinic acid, a step in which the presence of water is essential.

Oxidation of 3-Picoline. When V_2O_5 -pumice (51.84 to 100) was used as catalyst, the conversion of 3-picoline to nicotinic acid was 15.85% at 380° C., compared to 39.2% of isonicotinic acid in the case of 4-picoline. At higher temperatures, more carbon dioxide was formed. With a catalyst composition of V_2O_5 -MoO₃-pumice (33.06:5.83:100), a conversion of 15.5% to nicotinic acid was obtained with no carbon dioxide at 340° C. Above this temperature, much of the 3-picoline was oxidized to carbon dioxide. A number of catalysts with varying composition of V_2O_5 -MoO₃ were tried and the results obtained under the best conditions are given in Table IV.

Table III. Distribution of Oxidation Products with and without Use of Steam in Feed in Oxidation of 4-Picoline

Temperature 350 ° C., air rate 50 \pm 2 liters/hr. at 30 ° C. Picoline feed rate 1.2 to 1.3 g./hr., moles steam/mole 4-picoline 29 to 31

	% Conversion to						
	Isonicotinic acid	Diol (glycol)	Carbon dioxide	Unreacted, $\%$			
Catalyst.	V_2O_5 -Kies	elguhr, 51.	84 to 100				
Without steam With steam	52.5 71.6	29.1 12.6	3.5 4.7	8.3 8.6			
Catalyst. V_2	O5-Cr2O3-Ki	eselguhr, 5	1.84:5.18:	100			
Without steam With steam	51.2 68.1	29.6 12.6	9.6 8.3	9.6 9.2			

With increase in MoO_3 ratio the percentage conversion to nicotinic acid decreased. In all these cases the conversion to carbon dioxide was very high above 500° C. and the yield of nicotinic acid dropped rapidly. An increase in air-picoline ratio resulted in higher conversions to acid as well as carbon dioxide and an increase in space velocity resulted in decreased conversion.

Best results were obtained in the present reaction with a catalyst containing 90% V₂O₅ and 10% MoO₃. At 410° C., with a space velocity of 1650 and a molal ratio of 197.5, 37.4% 3-picoline was converted to nicotinic acid. The conversion to carbon dioxide under these conditions was also high. A change in the space velocity from 1650 to 4740 dropped the conversion to nicotinic acid from 37.4 to 14.43%.

Table IV. Comparative Efficiency of Catalysts in Oxidation of 3-Picoline

	Optimum	Conditions				
		Space velocity,	Molal	% Cont	ersion to	S. T. Y.,
Catalyst	Temp., ° C.	liters/hr./ liter	Ratio, Air/Picoline	Nicotinic acid	Carbon dioxide	G./Hr./ Liter
V_2O_5 -pumice, 51.84 to 100	400	1850	225	24.65	6,60	11.1
V_2O_5 -MoO ₃ -pumice, 33.06:5.83:100	400	1800	116	29.60	16.05	25.21
V_2O_5 -Mo O_3						
15 to 85	460	2240	185	21.20	27.40	14.1
23.8 to 76.2	480	2900	185	25.40	38.90	21.86
38.5 to 61.5	520	2000	185	22.8	48.0	13.5
70 to 30	480	2240	185	34.6	26.7	23.0
90 to 10	410	1650	197.5	37.4	20.95	17.15

Table V. Summary of Results Obtained with Various Catalysts in Oxidation of 3-Picoline in Fluidized Bed

	Optimu	m Conditions				
		Space velocity.	Molal	% Conv	ersion to	
	Temp.,	liters/hr./	Ratio, Air/	Nicotinic	Carbon	S. T. Y.,
Catalyst	° Ĉ. 1	liter	3-Picoline	acid	dioxide	G./Hr./Liter
V_2O_5 -pumice, 51.84 to 100	375	2395	225.6	16.65	9.74	9.65
Tin vanadate on pumice	320	1213	213.0	15.01	23.20	5.25
V_2O_3 -MoO ₃ -pumice, 33.06:5.83:100	400	2300	244.0	19.61	19.10	10.14
V_2O_5 -Fe ₂ O ₃ -pumice, 33.06:16.64:100	375	1250	210.0	18.52	29.44	6.73
V ₂ O ₅ -Cr ₂ O ₃ -pumice, 33.06:16.64:100	400	1177	242.9	20.12	34.20	5.35

Table VI. Summary of Results Obtained in Fixed and Fluidized Beds in Oxidation of 3-Picoline

		Space Velocity,	Molal Ratio		% Cont	ersion to
Catalyst	Type of Bed	Liters/Hr./ Liter	Air/3- Picoline	<i>Temp.</i> , ° Ĉ.	Nicotinic acid	Carbon dioxide
$\rm V_2O_5$ -pumice, 51.84 to 100	Fixed Fluidized	1850 2395	225 200	400 375	24.60 16.65	6.60 9.74
V_2O_5 -MoO ₃ -pumice, 33.06:5.83:100	Fixed	1800	116 230	400 400	29.60	16.05 19.10
$\mathrm{V_2O_5}$ (fused)-pumice, 70 to 30	Fixed Fluidized	4000 5004	84 200	500 490	26.60 24.37	38.60 23.01

Table VII. Relative Efficiency of Various Catalysts under Optimum Condition in Oxidation of 4-Picoline in Fluidized Bed



EFFECT OF THIRD COMPONENT ON ACTIVITY. Different metallic oxides were incorporated in the V_2O_5 -MoO₃ system and the activity of these ternary oxide catalyst systems was noted. The following compositions were prepared:

$$\begin{array}{l} V_2O_5\colon MoO_3\colon CoO,\ 80\colon 10\colon 20\\ V_2O_5\colon MoO_3\colon NiO,\ 85\colon 10\colon 5\\ V_2O_5\colon MoO_3\colon Ag_2O,\ 85\colon 10\colon 5 \end{array}$$

The data obtained reveal that the cobalt oxide-promoted catalyst was active at 365° C. and 13.8% nicotinic acid was obtained. Above 400° C., the catalyst became highly degradative, resulting in the production of carbon dioxide only. The nickel oxide-promoted catalyst showed more or less similar results, but the silver oxide-promoted catalyst was somewhat better.

Effect of Supports on V_2O_5 -MoO₃, 90 to 10 Catalyst. Aluminum oxide (calcined) and purified kieselguhr were

tried as supports for V_2O_5 -MoO₃, 90 to 10 catalyst in this reaction. The results obtained with Al_2O_3 -supported catalysts were not very different from those obtained with unsupported catalyst, particularly below 380° C. At higher temperatures total combustion was favored with the Al_2O_3 -supported catalyst. Kieselguhr as a support was a much more active catalyst than Al_2O_3 , but in this case also the activity of the catalyst favored the formation of carbon dioxide.

OXIDATION OF 3-PICOLINE OVER FUSED VANADIUM PENTOXIDE. Fused vanadium pentoxide was promising in the oxidation of 4-picoline to isonicotinic acid and was active in the oxidation of xylene to phthalic anhydride, as reported by Bhattacharyya and Gulati (7). But in the present reaction catalyst containing V_3O_5 (fused)-pumice, 70 to 30, showed little activity below 370°, and at 400° C. the conversion to nicotinic acid was only 9.25% as against 24.6% with the unfused catalyst. The conversion to acid increased very slowly up to 500° C., beyond which carbon dioxide was formed in excessive amounts.

Results of oxidation of 3-picoline to nicotinic acid in the vapor phase can be summarized as:

No other product, except traces of nicotinaldehyde, nicotinic acid, and carbon dioxide, could be identified in the products of reaction.

Vanadium pentoxide promoted with molybdenum oxide $(V_2O_5-MoO_3, 90 \text{ to } 10)$ was the best of all the catalysts containing vanadium oxide. A conversion of 37.5% of 3-picoline to nicotinic acid was obtained at 410° C. with a space velocity of 1650 liters per hour per liter and molal air-3-picoline ratio of 197.5. Addition of the oxides of cobalt, nickel, and silver to the above catalyst or use of supports led to degradative oxidation of 3-picoline to carbon dioxide.

The temperature at which the oxidation of 3-picoline starts is much higher than for 4-picoline and consequently much more 3-picoline is converted to carbon dioxide by oxidation. With rising temperature, the conversion to acid increases

With rising temperature, the conversion to acid increases until excessive oxidation to carbon dioxide starts, after which the yield of acid falls rapidly.

With increase in the molal ratio of air to 3-picoline, the conversion to nicotinic acid increases. An optimum molal ratio of about 200 moles of air per mole of 3-picoline was obtained in most cases.

The combustion to carbon dioxide could be appreciably reduced by increasing the space velocity, but the conversion to acid was lowered at the same time.

Oxidation of 2-Picoline. The vapor phase oxidation of 2picoline was studied by Mathes *et al.* (17) on a V_2O_5 -MoO₃ catalyst supported on SiO₂. Pyridine-2-aldehyde and 2pyridoin were reported as the chief products of oxidation. Ishiguro, Kimura, and Utsumi (7) oxidized 2-picoline over a nickel oxide-kaolin catalyst in the temperature range of 180° to 250° C. They reported 3.4 to 6.2% pyridine in the reaction product. Lewis and Brown (10) reported 18.8% conversion of 2-picoline to picolinic acid over a tin vanadate catalyst at 255° C. with an oxygen-picoline molal ratio of 9.

The main difficulty in the catalytic vapor phase oxidation of 2-picoline is the ease with which picolinic acid decarboxylates to pyridine. The acid begins to lose carbon dioxide at 160° C. The formation of pyridine in the catalytic vapor phase oxidation of 2-picoline has been reported by Ishiguro, Kimura, and Utsumi (7).

Another factor responsible for the poor yield of the acid is the speedy condensation of pyridine-2-aldehyde formed in the reaction to 2-pyridoin, probably under the influence of traces of hydrogen cyanide obtained by the thermal decomposition of 2-picoline at the high temperature used in the reaction.

Oxidation of 3- and 4-Picolines in the Fluidized Catalyst Bed

The apparatus used in the oxidation of picolines in the fluidized bed was similar to that described by Bhattacharyya and Kar (2).

Oxidation of 3-Picoline in Fluidized Bed. A large number of catalysts consisting of vanadium pentoxide, promoted with metallic oxides such as chromium trioxide, iron oxide, and molybdenum oxide, were tested. The results obtained with these catalysts under optimum conditions are summarized in Table V.

The results obtained under the optimum conditions with some of the active catalysts in fixed and fluidized bed operations are recorded in Table VI. The optimum temperatures in both cases (for highest conversions of 3-picoline) were nearly identical. In the fluidized bed, the optimum space velocity was slightly higher, which resulted in higher space-time yield. For each catalyst, the conversion to nicotinic acid was always higher in the fixed bed. Conversion to carbon dioxide was the same in both cases.

Oxidation of 4-Picoline in Fluidized Bed. The relative efficiencies of various catalysts containing vanadium pentoxide promoted with certain metallic oxides are recorded in Table VII. The optimum concentration of the promoter oxides was different for different systems studied. The percentage conversion to isonicotinic acid was maximum with the catalyst promoted with Cr_2O_3 , but this catalyst was much more degradative than the others. The iron oxide-promoted catalyst showed the highest selectivity for isonicotinic acid under optimum conditions, whereas molybdenum oxide as a promoter brought about a balanced effect as regards conversion, selectivity, and space time yield.

Table VIII compares the results obtained with various catalysts in fixed and fluidized beds. Since the oxidation of 4-picoline is an exothermic reaction, it was anticipated that fluidized bed operation would lead to higher yields. But from

Table VIII.	Comparative	Study of	of Results	Obtained	under	Optimum	Conditions	in Fixed	and	Fluidized	Beds	in	Oxidation	of
					4	-Picoline								

		Space Velocity,	Molal Ratio,		% Conversion to		
Catalyst	Type of Bed	Liters/Hr./ Liter	Air/4- Picoline	Тетр., ° С.	Isonicotinic acid	Carbon dioxide	
V_2O_5 -pumice, 51.84 to 100	Fixed Fluidized	2395 2380	231 138	340 320	41.40 29.20	2.40 19.10	
V ₂ O ₃ -MoO ₃ -kieselguhr, 31.09:2.74: 100 V ₂ O ₃ -MoO ₃ -pumice, 33.06:5.83:100 V ₂ O ₂ -Fe ₂ O ₃ -kieselguhr, 51.84:5.18:	Fixed Fluidized	2436 2096	171 142	360 360	47.36 35.67	6.80 11.68	
V_2O_5 -Fe ₂ O ₃ -pumice, 33.06:10.64:100 Fused V_2O_5 Fused V_2O_5 -pumice, 70 to 30	Fixed Fluidized Fixed Fluidized	2414 1766 1479 4229	154 210 166 190	320 360 380 435	48.94 37.43 39.15 27.26	7.95 11.14 1.10 15.45	

the experimental data it is clear that fixed bed operation gave much better yields of isonicotinic acid. This may be due to further oxidation of the products formed in the fluidized bed because of more intimate mixing with the catalyst and backmixing of the products, giving rise to the formation of undesirable carbon dioxide. In fact, the fluidized bed gave more carbon dioxide in most of the experiments conducted.

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OXIDATION OF SOME ORGANIC COMPOUNDS BY AN OXIDE OF ARSENIC, ANTIMONY, OR BISMUTH

Production of Methacrylaldehyde from Isobutyraldehyde and Other Oxidations

CHARLES W. HARGIS AND HOWARD S. YOUNG

Research Laboratories, Tennessee Eastman Co., Division of Eastman Kodak Co., Kingsport, Tenn.

Oxidation by an oxide of arsenic, antimony, or bismuth at elevated temperatures was found to create unsaturation alpha, beta to an unsaturated functional group in a variety of organic compounds. Water and reduced oxide are formed concurrently with the ethylenic compound. In some instances, depending on the oxidation resistance of the organic compounds involved, oxygen may be fed simultaneously to obtain a catalytic type of oxidation. The reaction was developed into a possible commercial synthesis of methacrylaldehyde from isobutyraldehyde.

DELABY and Demoulin reported vapor-phase isomerization of α,β -unsaturated alcohols to corresponding saturated ketones over nickel at 210° C. and over copper at 300° C. (7, 8). Later, Groll and Ott achieved vapor-phase isomerization of 2-methyl-2-propen-1-ol to isobutyraldehyde at elevated temperatures over copper and over porous catalysts such as silica and pumice (10). Both groups of investigators reported that isomerization was not complete. Thus, it is possible that the process is reversible, so that isobutyraldehyde could be converted to 2-methyl-2-propen-1-ol. This would be economically attractive, so we started to search for a catalyst for this reaction. In one experiment, isobutyraldehyde was passed over antimony(V) oxide at 320° C. Unexpectedly, the products were methacrylaldehyde, water, and a lower oxide of antimony.

Methacrylaldehyde is the starting point for the synthesis of numerous valuable compounds such as methacrylic acid and its esters (5, 15), polymers, and synthetic intermediates (1). Since isobutyraldehyde is readily available from hydroformylation of propylene, its conversion to methacrylaldehyde by the oxidative dehydrogenation route was further investigated. Tests of the other Periodic Group VA oxides showed that arsenic(V) oxide, antimony(IV) oxide, and bismuth(III)oxide also oxidized isobutyraldehyde to methacrylaldehyde when reaction temperatures were suitably adjusted. The

behavior of some other organic compounds in the presence of these oxides was also examined.

Experimental

Apparatus and Method. Reactions were carried out in the apparatus illustrated in Figure 1. Liquid feeds were delivered to the reactor through a Fischer and Porter Co. Flowrator under nitrogen pressure from a graduated reservoir. Gases were fed through capillary-type flowmeters.

Reactors. These were usually constructed from 33-inch lengths of 25-mm. o.d. Vycor tubing. The reactor used in the study of the preparation of methacrylaldehyde by a cyclic process was made of 38 mm. o.d. Vycor tubing. A steel block, heated by a three-element furnace equipped with automatic temperature controllers, was used to heat the reactors. Reactor heads were designed to permit simultaneous feeding of gases and liquid.

Procedure. Reactors were charged with granular oxidant which was positioned on a bed of Vycor chips so as to be heated by the middle element of the furnace. A layer of Vycor chips was placed on top of the oxidant bed to serve as a preheater and mixing section. The reactor was placed in the block in the furnace, and the oxidant was brought to the desired temperature in an air flow. The feed lines were connected. the system was flushed with nitrogen and pressurized with nitrogen to test for leaks, and the run was started. At the end of the production period, the reactor was flushed with nitrogen and the product was removed from the receiver and cold traps. In cyclic operation the oxidant was regenerated between production periods. In this case, product was re-