DEHYDROGENATION OF PIPERAZINE INTO PYRAZINE ON ALUMINA–PLATINUM CATALYSTS

G. V. Isagulyants, K. M. Gitis, V. A. Myasnikov,
and G. E. Neumoeva

UDC 541.128:542.941.8:547.861.3

Dehydrogenation of piperazine on alumina–platinum catalysts at 360-400°C was investigated. It was found that the alumina–platinum catalyst has low selectivity in the formation of pyrazine (yield ≤43%), and dehydrogenation is accompanied by decomposition and coke formation and products of decomposition in the formation of alkylpyrazines. The alumina–platinum catalyst in In_2O_3 and Re_2O_7 additives permits obtaining pyrazine with a yield of up to 80%. Dehydrogenation of piperazine is accompanied by reactions of decomposition, dehydroisomerization, and alkylation to a small degree, resulting in the formation of pyrrole, methylimidazole, and alkylpyrazines.

Pyrazine (II) and its alkyl-substituted homologs are used for preparation of drugs, insecticides, fluorescent dyes, and flavoring additives [1]. Dehydrogenation of piperazine (I) in the presence of oxide and supported metal catalysts is a common method of its preparation [2]. Of these catalysts, the platinum catalysts widely used in different dehydrogenation processes, including dehydrogenation of higher paraffins into olefins [3], aromatization of paraffin hydrocarbons [4], and finally, reforming of gasolines [5, 6], are of special interest. The comparative data show that platinum catalysts supported on Al_2O_3 are the most active and stable of the existing dehydrogenating catalysts. Nevertheless, dehydrogenation of (I) on a platinum catalyst has only been studied in [7], where the reaction was conducted in the pulsed mode at too low a temperature and on a sample with a support (refractory brick) inappropriate for dehydrogenation. It was possible to increase the yields of (II) and improve the selectivity of the process by using alumina–platinum catalysts and using the available experience in modifying them in other dehydrogenation processes.

RESULTS AND DISCUSSION

The results of the experiments on dehydrogenation of (I) on different alumina–platinum catalysts are reported in Table 1. The unpromoted catalyst (Cat-1) was not very efficient for dehydrogenation of (I). In conditions where the conversion attained 100%, the yield of (II) on this catalyst is <43%. The remainder are by-products including 32% coke and gaseous products and 25% alkylpyrazines. The low yields of pyrazine on this catalyst are thus due to its low selectivity, more precisely, the processes of decomposition and coke formation and the participation of the products of decomposition in alkylation of the pyrazine formed which intensely take place against the background of dehydrogenation.

Attempts were made to suppress the acid function of the catalyst by addition of K_2O (Cat-2) in order to reduce the side processes. This resulted in an increase in the yield of catalyzate and a decrease in the fraction of alkylpyrazines in it, so that the yield of (II) increased by 1.5 times compared to the unpromoted sample. In addition to alkylpyrazines, the by-products contained a small amount of pyrrole. The yield of (II) decreased slightly with an increase in the concentration of Pt to 2% (Cat-3), due to an increase in the yields of pyrrole and alkylpyrazines.

A significant increase in the yields of (II) (to 70%) was obtained by addition of In_2O_3 to the catalyst (Cat-4), which not only suppresses the acid function of the alumina–platinum catalyst, but also simultaneously increases its dehydrogenating activity [8, 9]. It is possible to obtain highly active catalysts by addition of In_2O_3 even when exhausted reforming

---

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1483-1488, July, 1990. Original article submitted June 22, 1989.

0568-5230/90/3907-1340$12.50

TABLE 1. Yield and Composition of Products of Transformation of Piperazine on Dehydrogenating Catalysts

Catalyst	T, °C	V, h^{-1}	X, wt. %	Yield, wt. %					Concentration in catalyzate, wt. %					
				catalyzate	piperazine	methyl-pyrazine	ethyl-pyrazine	pyrrole	pyrazine	methyl-pyrazine	ethyl-pyrazine	piperazine	pyrrole	unidentified products
Pt(0,6%) – Al_2O_3 (Cat-1)	360	0,70	38,2	86,5	15,2	6.2	2,4	–	17.6	7,5	2.8	71,4	–	0,7
»	400	0,72	59,2	72.5	23,8	2.3	0,3	–	32,8	7,3	1,1	56,9	–	1,9
»	400	1,59	52,5	75,4	21,1	5,8	сл.	–	28,0	7,7	сл.	63,0	–	1,3
»	400	0,35	100,0	68,2	43,0	10,6	14,6	–	63,0	15.6	21,4	–	trace	–
Pt(0,6%) – Al_2O_3 – K_2O(1%) (Cat-2)	400	0,35	100,0	76,8	63,1	5,1	7,0	1,5	82,2	6,6	9,1	–	2.0	–
Pt(2,0%) – Al_2O_3 – K_2O(1%) (Cat-3)	400	0,35	100,0	74,9	57,1	5,6	8.6	3.6	76,2	7,5	11,5	–	4.8	–
Pt(0,6%) – Al_2O_3 – In_2O_3(2%) (Cat-4)	400	0,35	100.0	82,3	68.9	4,7	6,5	2.2	83,7	5,7	7,9	–	2,7	–
AP-56 – In_2O_3(2%) (Cat-5)	400	0,35	100.0	84,1	71,2	4,7	6,2	2,0	84.7	5,6	7,3	–	2,4	–
AP-56 – In_2O_3(3%) (Cat-6)	400	0,35	100.0	86,1	73,2	5.0	6,5	1,5	85,1	5,8	7,5	–	1,7	–
Pt(0.6%) – Al_2O_3 – K_2O(1%) – Re(0,5%) (Cat-7)	400	0,35	100.0	79.6	72,2	2.3	4,1	0,9	90.7	2,9	5,2	–	1,1	–
Pt(0,6%) – Al_2O_3 – In_2O_3(2%) – Re(0,5%) (Cat-8)	400	0,35	100.0	84,3	78,7	1.6	3,5	0,6 *	93,3	1.9	4,1	–	0,7	–
Alumina-~~chromium~~-potassium (Ct-9)	400	0,35	100,0	67,6	36,2	9,8	11,8	4,6	53,6	14.5	17,4	–	6.8	7,6

---

*A fraction (bp 140-160°C, 20 mm Hg, yield of 4.5%) containing 2-methylimidazole, imidazole, and N-methylimidazole was separated in distillation.

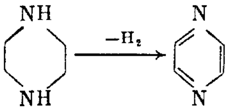
catalysts are used (Cat-5, 6). However, the amount of by-products on this catalyst is still relatively large (~11.5% alkylpyrazines and ~2.2% pyrrole).

Addition of Re caused a further increase in the selectivity of the catalyst, which permitted increasing the yield of (II) to an even greater degree. The simultaneous incorporation of In_2O_3 and Re_2O_7 was especially effective, increasing the yield of (II) to almost 80% while decreasing the yields of alkylpyrazines to 5.1% and pyrrole to 0.6% (Cat-8).

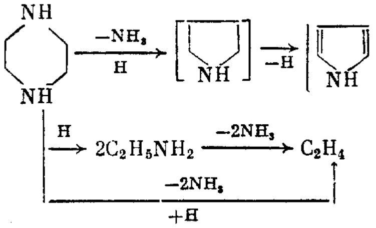
The data of dehydrogenation of (I) on an alumina–chromium–potassium catalyst [10] are also reported in Table 1. This catalyst was not very effective in dehydrogenation of (I): the yield of (II) on it was ≤38% for 100% conversion of (I) (Cat-9).

The $Pt–Al_2O_3–In_2O_3–Re_2O_7$ catalyst which exhibited the best results was used for preparative purposes. In distillation of a reaction mixture containing (II), alkylpyrazines, and pyrrole in addition to narrow fractions, another fraction was separated [bp 140-160°C, 20 mm Hg, yield of 4.5% for the starting (I)] which crystallized at ~20°C. The 2-methylimidazole was separated by recrystallization from benzene. In addition to it, this fraction contained unsubstituted imidazole and N-methylimidazole, with yields of 2.1, 0.9, and 0.05% for the starting (I), respectively. The NH_3 and $C_2H_5NH_2$ were separated from an aqueous solution containing absorbed gaseous products. The amount of NH_3 was equivalent to hydrogenolysis of ~5% of the starting (I) if both molecules of NH_3 were eliminated. The number of moles of $C_2H_5NH_2$ was ~50 times less than NH_3.

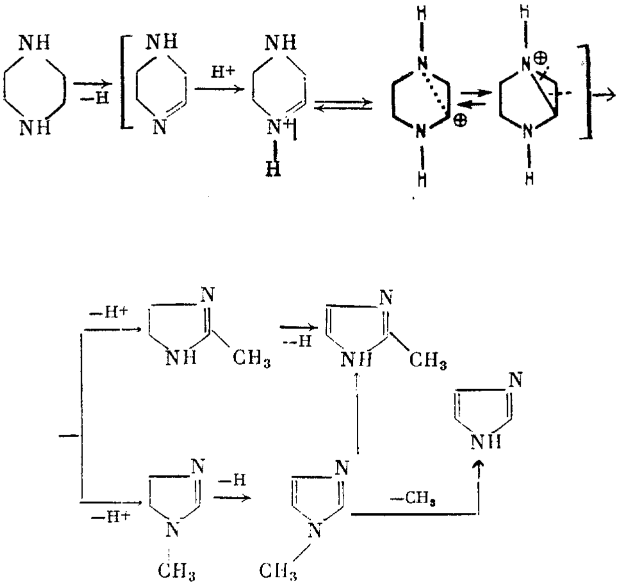
Thus, in addition to dehydrogenation (reaction I), (I) undergoes decomposition (deamination), dehydroisomerization, and alkylation on alumina–platinum catalysts. Schematically, these transformations can be represented as follows



(1)



(2)



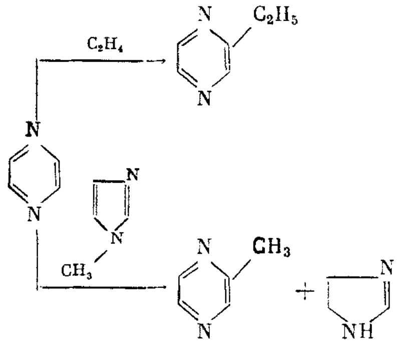
(3)

TABLE 2. Effect of the Nature of the Diluent Gas on the Yield of Pyrazine in Dehydrogenation of Piperazine on Modified Alumina–Platinum Catalysts (100% conversion)

Catalyst	T, °C	Diluent	Sampling time, h	Yield, wt. %		Coke, %
				catalyzate	pyrazine	
Cat-4	400	H_2	0–1	73,1	60,7	2,0
			1–2	82.3	68.9	
			2–3	80.0	66.7	
			3–4	76,2	63,5	
Cat-4	380	He	0–1	71,5	55,6	2,0
			1–2	77,1	62,5	
			2–3*	82,9	53,4	
			3–4†	81,5	51,8	
Cat-8	400	H_2	0–1	75,5	69,0	2.7
			1–2	84.4	78,7	
			2–3	86,7	81,6	
			3–4	82,7	76,9	
Cat-8	375	He	0–1	76,0	66,7	2,3
			1–2	79,2	72,8	
			2–3	90,4	82,2	
			3–4	82,8	78,1	

---

*Conversion of (I) of 96.9%.
†Conversion of 87.4%.



(4)

Incomplete deamination of the piperazine ring can result in ring narrowing and formation of pyrrole according to reaction (2), and complete deamination can cause formation of ethylene. Since the yield of pyrrole increases with an increase in the concentration of Pt from 0.6 to 2.0%, it is possible to hypothesize that decomposition of the piperazine ring takes place with the participation of Pt sites. The absence of pyrrole among the products of transformation of (I) on the unpromoted sample is due to the ease of its oligomerization under the effect of acids [11]. Addition of In_2O_3 suppresses the acidity of Al_2O_3, but the residual acid sites remain [12], and their strength is apparently sufficient for isomerization of the six-member ring into a five-member ring, which forms 1- or 2-methylimidazole after dehydrogenation [reaction (3)]. 1-Methylimidazole is easily demethylated or isomerized into 2-methylimidazole on Al_2O_3 [13]. Then (I) is alkylated with the formation of methyl- or ethylpyrazines [reaction (4)].

The stability of the catalyst is important for the practical implementation of the process. As noted above, the experiments on dehydrogenation of (I) were conducted in an atmosphere of H_2, whose role consists of reducing coke formation. However, introduction of H_2 is unfavorable in another respect, since the equilibrium is shifted, which requires increasing the temperature to obtain the same yields of (II). From this point of view, an inert gas which permits conducting the process at lower temperatures is preferred. The results of experiments on Cat-4 and Cat-8 conducted in an atmosphere of He and H_2 are reported in Table 2. On Cat-4, the yield of (II) in conducting the experiment in H_2 was almost constant during the entire four-hour experiment. When H_2 was replaced by He, the same yield of (II) was obtained at a lower temperature, but it decreased significantly during the experiment. At the same time, the yields of (II) in a He current were the same and were stable during the entire experiment on Cat-8, which contains Re_2O_7 in addition to In_2O_3. The elevated stability of this catalyst was also confirmed in conducting 12-hour experiments on dehydrogenation of (I).

EXPERIMENTAL

The experiments on dehydrogenation of (I) were conducted on a flow-type setup with a quartz reactor. Piperazine was admitted into the reactor in the form of vapors in a current of the carrier gas. The products of the reaction were collected in two sequentially connected containers cooled with ice and a mixture of dry ice and acetone, respectively, and the uncondensed products were bubbled through a Tishchenko flask with water. The experiments were conducted at 360-400°C and the volume flow rate of (I) (melt) was 0.35-1.59 h^{-1} with dilution with H_2 or He 7:1 (molar). The duration of the experiment was 1-4 h with hourly sampling of the products of the reaction for analysis.

The products were analyzed by GLC in a 3 m × 3 mm column; 1 wt. % PEG-20,000 supported on NaCl (0.15-0.25 mm fraction) was used as the stationary phase. The temperature of the analysis was 80°C, the carrier gas flow rate was 30 cm^3/min, FID. The products were identified by chromatography-mass spectrometry on a Varian MAT using the same chromatographic column. The composition of the products was also confirmed by the PMR spectra (Tesla BS-467 spectrometer, 60 mHz) of the narrow fractions separated from the catalyzate by distillation in a column with an efficiency of six theoretical plates. The mass spectra (MS) and PMR spectra of the products contained in the catalyzate are reported below (cf. [14]): pyrazine [MS, m/z: 80, 53, 40; PMR (δ, ppm): 8.63 s (4H)]; methylpyrazine [MS, m/z: 94, 67, 26; PMR (δ, ppm): 2.84 s (3H, 8.48 m (3H)]; ethylpyrazine [MS, m/z: 108, 107, 80; PMR (δ, ppm): 1.27 m (3H, J = 7.5 Hz), 2.99 q (2H, J = 7.5 Hz), 8.48 m (3H)]; pyrrole [MS, m/z: 67, 41, 40; PMR (δ, ppm): 6.39 m (2H); 7.01 m (2H)]; methylpyrrole [MS, m/z: 81, 80, 53]; 2-methylimidazole [(mp 140-142°C, PMR (CD_3OD, HMDS standard, δ, ppm): 2.27 s (3H), 6.80 s (2H)]; ethylamine [PMR (H_2O—CD_3OD, 9:1, δ, ppm): 1.54 t (3H), 2.87 q (2H)].

The composition of the catalysts studied is given in Table 1. Platinum was applied on γ-Al_2O_3 by impregnation of γ-Al_2O_3 grains with an aqueous solution of H_2PtCl_6 previously moistened with an aqueous solution of acetic acid. The remaining additives were added by successive impregnation with aqueous solutions of KOH, $In(NO_3)_3 \cdot 4.5H_2O$, or $(NH_4)_2Re_2O_7$ with intermediate crying at 140-160°C for 6 h. The catalysts prepared in this way were calcined in an air current at 550°C for 4 h. The alumina—chromium catalyst contained 15 mole % Cr_2O_3 and 85 mole % Al_2O_3, to which 1 wt. % K_2O was then added.

LITERATURE CITED

1. G. W. H. Cheeseman and E. S. G. Wertiuk, Advances in Heterocyclic Chemistry, Vol. 14, Academic Press, New York—London (1972), p. 104; G. B. Barlin, in: The Chemistry of Heterocyclic Compounds, A. Weissberger (ed.), Vol. 41, Interscience, New York (1982), p. 8.
2. USA Patent No. 3,005,820, Chem. Abstrs., 56, 7335d (1962); Japanese Patent No. 52-956 [7656.479], Chem. Abstrs., 86, 29872x (1977); USSR Inventor's Certificate No. 523,898, Byull. Izobret., No. 29, 66 (1976); M. Inoue, S. Enomoto, and J. Imamura, J. Pharm. Soc. Jpn., 95, 849 (9175); US Patent No. 2,580,221, Chem. Abstrs., 46, 6673a (1952).
3. N. R. Bursian, S. B. Kogan, V. Sh. Gruver, and P. N. Borutskii, Promoted Platinum Catalysts in Isomerization and Dehydrogenation of Paraffin Hydrocarbons [in Russian], TsNIITENeftekhim, Moscow (1981).
4. G. V. Isagulyants, M. I. Rozengart, and Yu. G. Dubinskii, Catalytic Aromatization of Aliphatic Hydrocarbons [in Russian], Nauka, Moscow (1983), p. 86.
5. G. N. Maslyanskii and R. N. Shapiro, Catalytic Reforming of Gasolines [in Russian], Khimiya, Leningrad (1985).
6. N. S. Kozlov, G. M. Sen'kov, V. A. Polikarpov, and V. V. Shipikin, Reforming Catalysts [in Russian], Nauki i Tekhnika, Minsk (1976).
7. J. C. Nigam, J. Chromatogr., 24, 188 (1966).
8. N. R. Bursian, S. B. Kogan, G. I. Semenov, and E. A. Levitskaya, Kinet. Katal., 15, 1608 (1974).
9. A. P. Tyupaev, E. A. Timofeeva, and G. V. Isagulyants, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2089 (1982).
10. M. I. Rozengart and B. A. Kazanskii, Usp. Khim., 40, No. 9, 1537 (1971).
11. Comprehensive Organic Chemistry, D. H. R. Barton and W. D. Ollis (eds.), Vol. 4, Pergamon Press, Oxford (1979).

12. S. B. Kogan, A. M. Moroz, O. M. Oranskaya, et al., Zh. Prikl. Khim., 56, No. 8, 1884 (1983).
13. M. R. Grimett, Adv. Heterocycl. Chem., 12, 164 (1970).
14. A. Cornu and R. Massot, Compilation of Mass Spectral Data, Presses Univ., Paris (1966); F. Uchimaru, S. Okada, A. Kosasayama, and T. Konno, J. Heterocycl. Chem., 8, 99 (1971).

MECHANISM OF OXIDATION OF CYCLOHEXANE BY THE RADICAL CATION OF PYRIDINE N-OXIDE

S. I. Kulakovskaya, S. N. Shamaev,
and V. M. Berdnikov

UDC 541.124:542.943:547.592.12:
541.515-128.4:547.823

Oxidation of pyridine N-oxide in the presence of cyclohexane was studied on platinum and carbon glass rotating disk electrodes using the method of cyclic voltammetry in 0.2 N $LiClO_4$ in acetonitrile. It was hypothesized that the electrochemically generated N-oxide radical cation reacts with cyclohexane according to the mechanism of hydrogen atom cleavage.

To explain the unusual selectivity of oxidation of some hydrocarbons in systems of the "Zhif" type, it was hypothesized in [1] that the particle $PyO^{\dot{+}}$ which can be considered an oxygen cation solvated by a base capable of transporting O^+ to the organic substrate, is formed in them. The data obtained in studying electrochemical oxidation of pyridine N-oxide on platinum and carbon glass (CG) electrodes in acetonitrile in the presence of cyclohexane are reported in the present communication; they permit judging the possible mechanism of the reaction of $PyO^{\dot{+}}$ with the cyclohexane molecule.

EXPERIMENTAL

The method of the rotating disk electrode (RDE) prepared from platinum or CG and the method of cyclic voltammetry were used in the electrochemical experiments. A number of details of the experimental method was described previously [2]. A PI-50-1 potentiostat with a PR-8 programmer was used for recording the polarization curves, and an ESM-700 electrochemical measurement system (GDR) was used for recording the cyclic voltammograms. The electrode areas were equal to 0.07 cm^2 (Pt) and 0.181 cm^2 (CG). The reference electrode was an aqueous normal calomel electrode (n.c.e.) separated from the cell by a transition bridge filled with 0.2 N $LiClO_4$. The potentials are reported with an error of ±10 mV. All measurements (except for specially mentioned cases) were conducted in an atmosphere of argon (special purity).

RESULTS AND DISCUSSION

One-electron oxidation of pyridine N-oxide on Pt or CG RDE takes place irreversibly for $E_{1/2} = 1.72$ V, and the limiting current has a diffusion character [2]. In the 0.0 to 2.1 V potential range, cyclohexane is not oxidized on either Pt or on CG electrodes. However, when cyclohexane is added to a solution containing 10^{-3} M PyO and 0.2 N $LiClO_4$ in CH_3CN, a decrease is observed in the limiting current of oxidation of PyO, manifested more clearly in each successive recording of the voltammograms (Fig. 1). The higher the concentration of cyclohexane, the more sharply this effect is manifested. For a concentration of $C_6H_{12} \geq 5 \cdot 10^{-3}$ M, the voltammograms acquire a hump-shaped form which could be due to adsorption of the product of the chemical reaction following the electrode process. In our experiments, the electrodes underwent two alternate polarizations for 20 sec at 1.5 and 0.0 V before recording each voltammogram. Since this pretreatment does not eliminate the effect of inhibition, it is possible to hypothesize that strong chemisorption of a substance which is the product of the

---

N. N. Semenov Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka Branch. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1488-1491, July, 1990. Original article submitted March 23, 1989.