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TPD–TPR–MS Mechanistic Study of the Synthesis of 2-Methylpyrazine over Palladized Zn–Cr Oxide

LUCIO FORNI[1] AND PAOLO POLLESEL

Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Via C. Golgi 19, 20133 Milano, Italy

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A mechanistic study of the cyclization of ethylenediamine (ED) and propyleneglycol (PG) to 2-methylpyrazine is reported, carried out by means of the TPD–TPR–MS technique. The reacting system proved to be complex, due to the presence of numerous intermediates and by-products, deriving either from one of the two reactants, or from both. The optimal reaction temperature, permitting the best selectivity to the desired product, was about 660 K. At least two different types of surface sites are present on the catalyst, and only the higher-energy ones activated the reactants. The reaction probably involves a rate-determining step of the Rideal–Eley type, between adsorbed PG and ED coming from the gaseous phase. This step leads to a fully hydrogenated intermediate, 2-methylpiperazine, which quickly dehydrogenates and aromatizes to 2-methylpyrazine.

INTRODUCTION

In some previous papers (*1–6*) we reported extensively on a catalytic two-step route for the preparation of 2-amidopyrazine. The first step consists of the cyclization of ethylenediamine (ED) and propyleneglycol (PG) to 2-methylpyrazine (MP), taking place on a Pd/Zn–Cr–O catalyst at 623–703 K, atmospheric pressure, and in the presence of an excess of steam (*2, 4, 5*). The second step is the ammoxidation of MP to 2-cyanopyrazine, on a different catalyst (*1, 3, 6*). The mechanism of the second step has been studied by TPD–TPR–MS and the results are reported in a companion paper (*7*). We report here on a mechanistic study of the first step, namely the catalytic cyclization of ED and PG, by means of the same experimental technique.

EXPERIMENTAL

Catalysts. The best catalyst for this reaction was found and optimized in the previous screening investigation (*2, 5, 8*). It consists of a mixture of Zn and Cr oxides, prepared by coprecipitation, drying, calcination, and impregnation with aq. Pd sulfate. The composition and the main physico-chemical characteristics of our catalyst, here referred to as B3, are summarized in Table 1. However, many runs, especially most of the preliminary ones, were carried out on a commercial catalyst, Harshaw Zn-0312T, of very similar composition, apart from Pd. The physico-chemical properties of the commercial catalyst are given in the same Table 1, together with some typical activity data, referring to identical reaction conditions, for comparison.

Procedure. A detailed description of the experimental apparatus employed is given in the companion paper (*7*). Different procedures were followed for the collection of experimental data, depending on the information desired. Such procedures have been defined after proper sets of preliminary experiments, aimed at defining the correct range of values of the experimental parameters, within which reproducible and reliable data could be collected in the various cases. Fresh catalyst samples were charged for every run.

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[1] To whom correspondence should be addressed.

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TABLE 1

Principal Characteristics of the Catalysts Employed

Catalyst	Zn-0312T	B3
Zn/Cr (atomic ratio)	3 : 1	3 : 1 + (1% Pd)
BET surface area (m^2/g)	130	52.9
Pore volume (cm^3/g)	0.2	0.4
Bulk density (g/cm^3)	1.55	1.12
Particle size (mm)	0.15–0.18	0.15–0.18
Conversion (mol% of fed ED)	81.9	75.5
Selectivity (mol% of converted ED)	43.9	75.2

Note. Reaction conditions: 663 K, atmospheric total pressure, ED/PG = 1/1 molar feeding ratio, continuous tubular reactor.

When working with the Zn-0312T catalyst, before the run a TPD ramp (20 K/min) was always carried out up to the maximum temperature attained in the present work and under a slow He flow, to avoid possible structural modifications of the catalyst during data collection. The usual operative conditions for the experiments including a TPD ramp were: catalyst charge 100 mg, carrier-gas (He) flow rate 20 cm^3/min, heating rate 20 K/min, initial isotherm 373 K, final isotherm 773 K. In a few cases a final 823 K isotherm was attained. Pulses (6 to 15 μl, 1 μl = 1 mm^3) either of pure ED, or pure PG, or of a mixture of the two (ED/PG molar ratio = 0.7) were injected during the initial isotherm. The operative conditions for the experiments carried out in isothermal mode were: catalyst temperature 623, 643, 663, or 683 K, pulse volume 3 to 5 μl, number of pulses 2 to 3.

When working with B3 catalyst, an activation by reduction before use was needed. Such a reduction was made *in situ* and consisted in flushing the solid with 10 vol% H_2 in He for 30 min at 593 K. This permitted avoidance of hot spots, the reduction being highly exothermic. After activation the reducing gas mixture was replaced by pure carrier gas and the catalyst was heated to the highest experimental temperature. The operative conditions with B3 catalyst were the same as those adopted with Zn-0312T, both in TPD and isothermal mode. Furthermore, some additional experiments were carried out with B3 catalyst by preadsorbing one of the reactants before the other. In these series of tests the reactants were preadsorbed through three 5 μl pulses as usual, either at different times or at different temperatures, the latter in any case exceeding the boiling point of the reactant, e.g., 398 K for ED and 473 K for PG. The preadsorption was followed by the usual TPR ramp up to 823 K. Finally a series of runs was conducted by preadsorbing one reactant, followed by TPD ramp with pulse of the other reactant. The scheme of these transient-response experiments was:

group a: (1) three 5-μl pulses of ED at 398 K
(2) 398–823 K TPD ramp with a 5-μl pulse of PG
(3) 3.75-min isotherm at 823 K
group b: (1) three 5-μl pulses of PG at 473 K
(2) 473–823 K TPD ramp with a 5-μl pulse of ED
(3) 2.5-min isotherm at 823 K.

The final short isotherm at the end of the ramp was needed in order to clean up the catalyst surface from any organic residue.

The tests were repeated several times, in order to monitor all the fragments forming, since no more than 10 different amu values can be monitored simultaneously with our apparatus (*7*).

RESULTS AND DISCUSSION

The desired information was obtained by monitoring the species desorbing during the TPD ramp, or after the pulses injected during the isothermal runs, as described in detail in Ref. (*7*). The attribution of the mass fragments to the various species has been done by comparison with mass-spectral data from the literature (*9, 10*). The experiments carried out by employing the pure reactants were aimed at obtaining information about the nature of the by-products coming from each one of them separately; those made by employing their mixture were aimed at throwing light on the activity of the catalyst

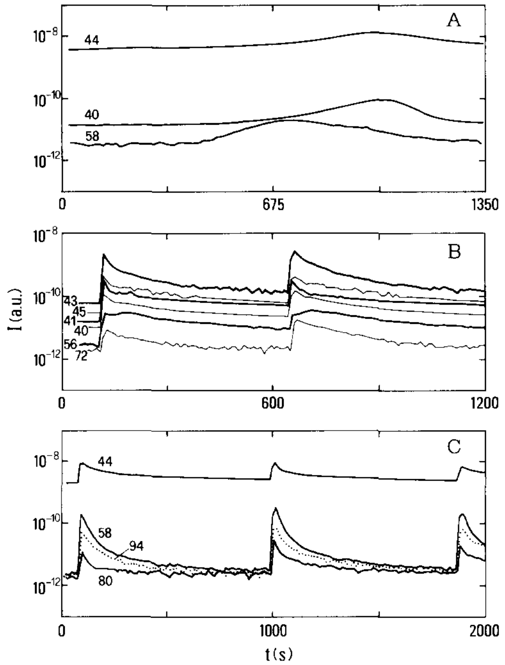

FIG. 1. (A) Example of a 373–823 K TPD ramp after preadsorption of PG on Zn-0312T catalyst. (B) Example of the spectra obtained with two pulses (5 and 3 μl, respectively) of PG in isothermal conditions (663 K). Zn-0312T catalyst. (C) Typical trend of some species detected and monitored after pulses of ED + PG mixture under isothermal conditions (663 K). Zn-0312T catalyst. Figures indicate the amu values of the spectrum.

as well as on the mechanism of the cyclization reaction.

A. Tests with Zn-0312T Catalyst

Typical examples of the spectra monitored during a TPD experiment, carried out after presaturation of the catalyst with one of the pure reactants or during isothermal experiments with injection of a pure reactant or of the mixture of the two, are shown in Fig. 1 (A, B, and C, respectively).

The runs carried out by injecting PG showed the formation of some by-products coming from the diol only. The temperature T_{max}, corresponding to the top of the desorption peak of the various species, is given in Table 2. The attribution of the signals to the different compounds presents some problems because of the simultaneous presence of many mass fragments in the spectra of various substances. However, the presence of the following species is certain: PG, ethanol, propanol, allyl alcohol, and acetone. The presence of propane and propene is less certain, since their characteristic mass fragments (amu = 39 and 41) are common to many other molecules.

TABLE 2

T_{max} of the Desorption Peaks after PG Preadsorption

Species	T_{max} (K)	Species	T_{max} (K)
H_2	573 and 723	Allyl alcohol	703
C_1 fragments	653 and ≃773	Propylene glycol	713
Water	573	Propanol	683
Ethanol	553 and 693	Acetone	613

Note. When two temperatures are reported, two desorption peaks were recorded (Zn-0312T Catalyst).

It can be noted that PG (T_{max} 713 K, see Table 2) has a good affinity for this type of catalyst, while acetone desorbs with a lower T_{max}. The highest T_{max} was observed for amu = 14 and 15 (C_1 fragments).

The runs carried out under isothermal conditions (663 K) gave peaks of the mentioned species, together with a peak for amu = 72, that was assigned to methylethylketone. The latter can form from ethanol and propanol, which in turn derive from PG (vide supra). Furthermore, a strong peak for acetone was observed, confirming that this species is an important product of the reaction. It can form from PG by dehydration. Indeed, it is well known (*11–13*) that dehydration is one of the most typical functions of Zn–Cr–O catalysts.

The TPD ramps after preadsorption of ED showed the desorption curves of ED, together with a neat peak of pyrazine (amu = 80 and 53). This was confirmed by the isothermal runs at 663 K. It may be concluded that, at this temperature and under the present reaction conditions, a large part of ED is quickly transformed into pyrazine. The isothermal runs showed also peaks for amu = 81 and 82, indicating the presence of methylpyrrole. This species was recognized also during a parallel mechanistic study of the cyclization ED + PG → MP (*14*).

Furthermore, the experiments with ED alone did not show clearly the presence of tetrahydropyrazine (THP), a kinetic intermediate for the reaction 2 ED → pyrazine, detected in very small traces in the cited work (*14*). Nevertheless, the formation of variously hydrogenated pyrazinic species must be assumed, since the peaks for amu = 41 were always more intense than those for amu = 43, in spite of the fact that the amu = 43 fragment is more important than the 41 fragment in the mass spectrum of ED. By considering that 41 is a typical fragment of the pyrazinic species, we must assume the formation of pyrazinic-ring derivatives.

The tests performed by injecting the ED + PG mixture were aimed at obtaining information about the formation of the principal products and about the most favorable temperature for the main reaction. In correspondence with the pulses (see, e.g., Fig. 1C) one can note the amu = 94 signal, the parent peak of the desired product MP. Strong peaks of acetone can also be observed, together with weaker peaks for amu = 80, indicating the formation of pyrazine. Two subsequent pulses of the ED + PG mixture at 663 K, the first one of 5 μl and the second of 3 μl, showed that the peaks of MP, pyrazine, and acetone for the second pulse were greater than those for the first, while the peak area of ED and PG was in line with the relative amount of the injected mixture. This fact suggests a process in which the products forming after the first pulse remain in part adsorbed on the catalyst and are removed by the successive pulse. An experiment with a sequence of three pulses of 5, 3, and 5 μl, respectively, showed that the signals relative to the various products increase after the second pulse and remain practically unchanged after the third one. This confirms that the MP (and probably the other species) formed after the former pulses is removed by the subsequent ones and that the species one sees in part form from the newly injected reactants and in part are simply desorbed.

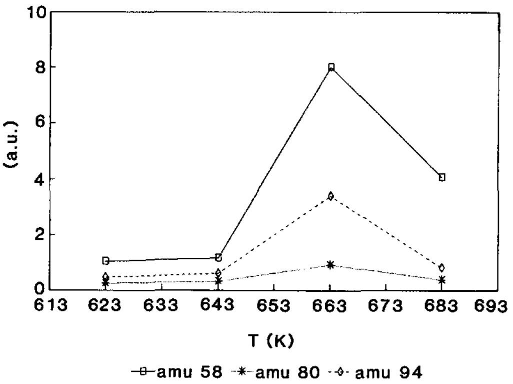

FIG. 2. Peak area of MP, pyrazine, and acetone (amu = 94, 80, and 58, respectively) obtained with isothermal pulses of ED + PG vs temperature. Zn-0312T catalyst.

The experiments carried out isothermally at different temperatures (Fig. 2) confirm that the highest selectivity to the desired product can be obtained at ca. 660 K, as found in our previous work (*1, 5*). However, by simply comparing peak areas, Fig. 2 data indicate acetone, instead of MP, as the product forming in larger amount. Nevertheless, we must remember that: (i) the apparatus used in the present study is very different from the plug-flow reactor employed in industrial application, (ii) these experiments are intrinsically of unsteady type, and (iii) all the present runs have been carried out in the absence of steam.

Finally, a further confirmation of the tendency of the products (especially MP) to remain adsorbed on the catalyst surface is given by the trend of the MP peak area vs the number of successive small identical pulses during the same run (Fig. 3). Indeed, the figure shows that the amount of product detected increases with the number of the injection at any temperature.

B. Tests with B3 Catalyst

Table 3 summarizes the series of the experiments carried out with separate and suc-

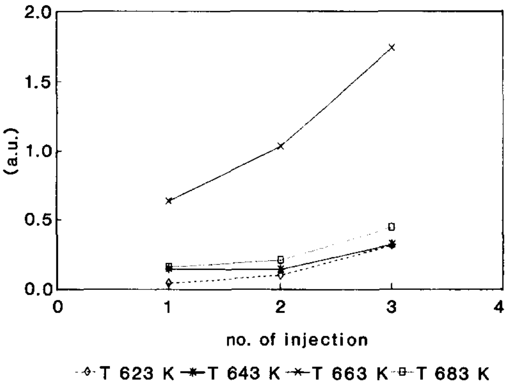

FIG. 3. MP peak area vs No. of subsequent pulses of ED + PG at different temperatures. Zn-0312T catalyst.

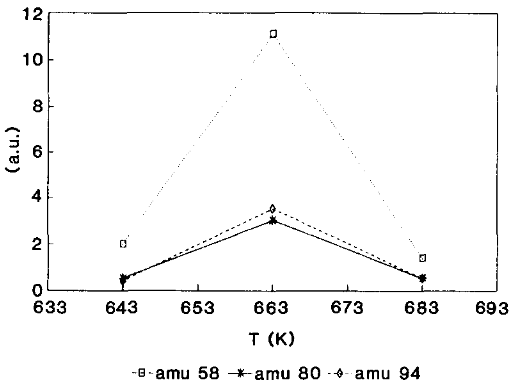

FIG. 4. MP, pyrazine, and acetone peak area after identical pulses of the ED + PG mixture under isothermal conditions, vs temperature (B3 catalyst).

cessive preadsorption of ED and PG, followed by the TPD ramp. During the ramp the desorption peaks of MP, pyrazine, and acetone were always observed, confirming the activity of the catalyst. The peak area of the desired product (MP) is also shown in the table.

The series made with the ED + PG mixture in isothermal conditions includes three runs, each one with three 5-μl pulses, carried out at 643 to 683 K. The formation of MP, pyrazine, and acetone has been observed in each case. The peak areas for the corresponding amu signals (94, 80, and 58, respectively) are shown in Fig. 4.

In the cited study (*14*) on the mechanism of the present reaction, the presence of some intermediate species and secondary products has been hypothesized and a series of steps leading from ED + PG to MP has been proposed for the main reaction. Such steps include the formation of the saturated heterocyclic ring 2-methylpiperazine, which dehydrogenates and aromatizes to MP through a pathway including tetrahydro- and dihydro-2-methylpyrazine (Fig. 5). The present transient-response pulse tests were then carried out aimed at detecting such intermediates before their transformation into the final product.

TABLE 3

Scheme of the Runs on B3 Catalyst with Separated Preadsorption of ED and PG

Experiment	amu 94 peak area (au)
1: ED at 463 K—2: PG at 463 K—3: ramp	6.63×10^{-10}
1: PG at 463 K—2: ED at 463 K—3: ramp	1.29×10^{-9}
1: ED at 398 K—2: PG at 473 K—3: ramp	1.10×10^{-9}
1: PG at 473 K—2: ED at 398 K—3: ramp	3.18×10^{-9}

The desorption peaks of MP, pyrazine, and acetone, obtained after preadsorption of ED + PG, followed by the TPR ramp, showed T_{max} = 603, 593, and 643 K, respectively. However, when preadsorbing pure MP or acetone, followed by TPD, T_{max} values of 533 or 423 K, respectively, were recorded, i.e., considerably lower. It can be deduced that at least two different types of site are present on the catalyst surface, as observed also for the Sb–V–Mn–O catalyst for the ammoxidation of MP to 2-cyanopyrazine (*7*). On the lower-energy sites, the species adsorb and desorb unaltered, while on the higher-energy ones the reactants adsorb and are activated for the transformation into products.

As for the experiments with separated adsorption of the reactants, referring to Table 3 data, one can see that the amount of MP forming after preadsorption of the reactant at two different, but lower temperatures, is

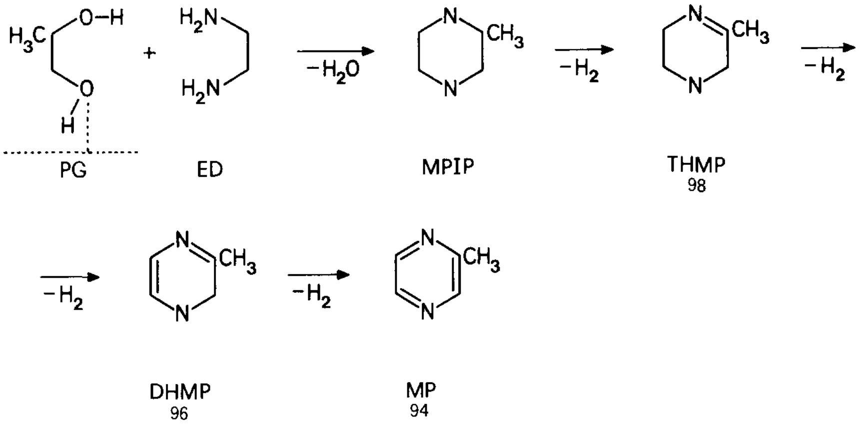

FIG. 5. Reaction pathway for the synthesis of MP (Ref. (*14*)).

larger than that obtained with preadsorption at higher temperature. However, a most interesting result is that a larger amount of MP formed when PG was preadsorbed before ED, than when ED preceded PG in adsorption. This occurred in all such runs, either with preadsorption of both the reactants at 463 K, or when they were preadsorbed at different temperatures. This confirms the proposal in another previous work (*15*), namely that, at a sufficiently low concentration of the reactants, when the competition for adsorption is less remarkable, the rate-determining step of the reaction is probably of the Rideal–Eley type, between adsorbed PG and ED coming from the gaseous phase.

Coming to the experiments with pulses of the ED + PG mixture under isothermal conditions, the most suitable temperature for the desired reaction was found to be ca. 660 K also with the B3 catalyst. However, it is interesting to compare the values of the peak area obtained with the two catalysts (Table 4). With respect to Zn-0312T, the palladiated catalyst (B3) leads to a small increase in selectivity to MP, but to a selectivity to pyrazine more than three times higher and to a comparable selectivity to acetone. This means that, over B3 catalyst, a lower amount of PG transforms into acetone, so that a larger amount of it can react with ED to give MP. Indeed, the higher formation of pyrazine, with respect to MP, is due to the easy decomposition of MP to pyrazine, owing to the absence of steam (*2*, *8*). Thus, the decreasing of the 58/(80 + 94) amu peak area ratio (last line of Table 4) confirms that the selectivity to pyrazinic species improves using the B3 catalyst, as shown by the continuous reactor experiments (Table 1).

The experiments with a pulse of one reactant during the desorption of the other (Table 5) proved to be useful in detecting the intermediates of the principal reaction. From the group a tests (pulse of PG during the desorption of ED), besides the usual MP, pyrazine, and acetone, the following species were detected: tetrahydropyrazine (amu = 84), dihydromethylpyrazine (96), and tetrahydromethylpyrazine (98), confirming the general pathway shown in Fig. 5. Nevertheless, no trace of methylpiperazine

TABLE 4

Peak Area (au) of the Products Obtained with Pulses of the ED + PG Mixture at 663 K

Species (amu value)	Zn-0312T	B3
Acetone (58)	8.01×10^{-9}	1.11×10^{-8}
Pyrazine (80)	9.21×10^{-10}	3.03×10^{-9}
MP (94)	3.40×10^{-9}	3.52×10^{-9}
58/80 ratio	8.70	3.66
58/94 ratio	2.36	3.15
58/(80+94) ratio	2.01	1.69

TABLE 5

Area (au) of the Most Important Desorption Peaks Obtained with Injection of One Reactant during the TPD Ramp following the Preadsorption of the Other Reactant (a) PG after ED, (b) ED after PG

amu	B3 catalyst		Zn-0312T catalyst	
	a	b	a	b
58	2.73×10^{-8}		2.63×10^{-8}	
84	1.07×10^{-10}		1.36×10^{-10}	
94	4.38×10^{-9}	2.09×10^{-9}	4.10×10^{-10}	7.50×10^{-10}
96	2.26×10^{-10}		1.24×10^{-10}	
98	6.88×10^{-11}		1.21×10^{-10}	
107		1.50×10^{-10}		5.19×10^{-11}
108	1.78×10^{-10}	1.74×10^{-10}	7.25×10^{-11}	1.72×10^{-10}

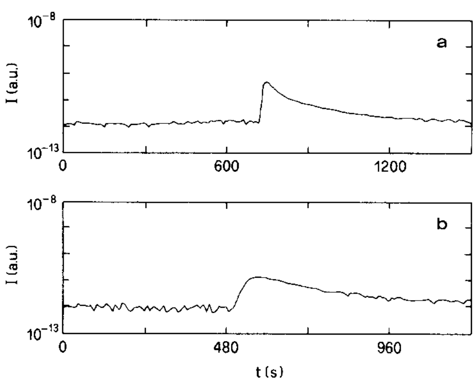

FIG. 6. Peaks of MP forming in correspondence with the pulse of (a) PG, during desorption of ED, (b) ED, during desorption of PG.

(amu = 85), the first intermediate of the reaction, was ever observed. This fact confirms that methylpiperazine dehydrogenates so quickly to the less hydrogenated species of the sequence, to be hardly recognizable (*14*). In some tests we observed also a small peak for amu = 108, that could be assigned to a secondary product, 2,5-dimethylpyrazine. The fragment with amu = 108 is present also in the mass spectrum of pyrazin-2-carboxy-aldehyde, but together with an important fragment at amu = 107, which was never detected in any of these groups of tests.

Group b experiments showed some important differences. The shape of the MP peak, obtained in correspondence with the pulse of the second reactant (ED) was smoother (Fig. 6). This confirms that a different mechanism is to be assumed for the two groups of runs. When ED is injected during the TPD of preadsorbed PG (group b) the reaction can proceed quickly through the Rideal mechanism. When the reversed sequence is followed, the injected PG must adsorb and remove a part of the preadsorbed ED, before the latter, now coming from the gas phase, can react with it. Furthermore, the partially hydrogenated pyrazinic species have not been detected in the group b experiments. This fact further supports the hypothesis of the Rideal mechanism, the reaction being so quick in group b runs that the intermediates can no longer be detected. Peaks for amu = 107 and 108 have been observed during these tests, indicating the presence of pyrazin-2-carboxyaldehyde. A possible pathway for the formation of the aldehyde was suggested elsewhere (*14*).

As for the parallel tests with the industrial catalyst, it can be noted (Table 5) that the amount of MP (amu = 94) forming with this catalyst is lower than with B3, by almost one order of magnitude. Nevertheless, the behavior of the reacting system with the two catalysts appears to be similar, except for the amount of some intermediates in group a experiments (see, e.g., Fig. 7). This is due

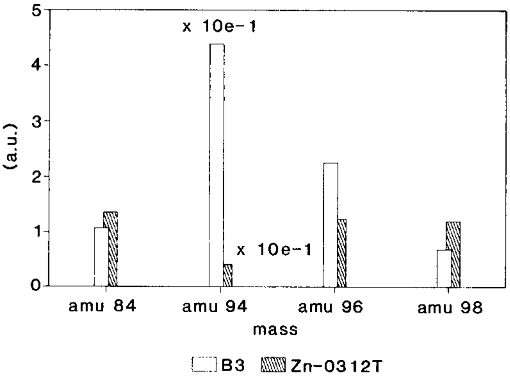

FIG. 7. Peak area of tetrahydropyrazine, MP, dihydromethylpyrazine and tetrahydromethylpyrazine (amu = 84, 94, 96, and 98, respectively) obtained in group a experiments with the two catalysts.

to the presence of Pd in the B3 catalyst, which favors dehydrogenation and successive aromatization. Hence, a larger amount of the less dehydrogenated species (tetrahydromethylpyrazine and tetrahydropyrazine, amu = 98 and 84, respectively) is noted with the Zn-0312T catalyst.

CONCLUSIONS

The principal conclusions we can draw from the present work can be summarized as follows: (i) The reacting system is much more complex than one can forecast from the very simple apparent reaction equation $ED + PG \rightarrow MP + 3H_2 + 2H_2O$. This is due to the presence of many intermediates and by-products, deriving either from one reactant or from both. (ii) The optimal reaction temperature, leading to the highest selectivity to the desired product, is about 660 K. (iii) The main reaction products show a strong tendency to remain adsorbed on the catalyst surface. (iv) At least two different types of sites are present on the latter. On the lower-energy sites reactants and products adsorb and desorb unaltered, while only the higher-energy sites are able to activate the reactants for both the main reaction and the reactions leading to undesired by-products. (v) Our B3 catalyst, in comparison with the industrial one, reduces the degradation of PG to acetone, probably by enhancing effectively the rate of cyclization to heterocyclic products. (vi) At least at low surface coverage, the rate-determining step of the process is of the Rideal–Eley type between adsorbed PG and gaseous ED and the reaction proceeds through the formation of an intermediate, fully hydrogenated species (methylpiperazine), which quickly dehydrogenates and aromatizes to MP.

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