THE STAGED SYNTHESIS OF 2-METHYLIMIDAZOLE FROM ETHYLENEDIAMINE AND ACETIC ACID IN THE PRESENCE OF A BIFUNCTIONAL ALUMINOPLATINUM CATALYST

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An investigation has been conducted into the staged synthesis of 2-methylimidazole from ethylenediamine and acetic acid in the presence of a bifunctional aluminoplatinum catalyst. It has been shown that the formation stage of 2-methylimidazoline occurs more quickly on γ -Al₂O₃ than its dehydrogenation on the Pt centers. From a comparison of the processes of dehydrogenation of 2-methylimidazoline in the molten phase and in aqueous solution it follows that the water eliminated in the imidazoline formation stage could cause the decrease in activity during the dehydrogenation on the Pt centers. The structures of the secondary and intermediate products have been established for each stage of the process and their formation routes are discussed.

Keywords: aluminoplatinum catalysts, bifunctional catalysis, alkylimidazoles, 2-methylimidazole.

The synthesis of C-alkylimidazoles form 1,2-diamines and carbonyl acids in the presence of bifunctional catalysts [1-5] is presently of considerable interest in terms of its practical implementation. The chemical reaction can be represented by the following scheme:



Bifunctional aluminoplatinum catalysts are extremely effective in this process, enabling various C-alkylimidazoles to be obtained selectively in high yields [1, 5, 6]. Results from a study of the synthesis of 2-methylimidazole (2-MII) from ethylenediamine and acetic acid [7] indicate that the slow stage of the process is the dehydrogenation of imidazoline (2-MIn) to 2MII. In this present study we have identified the slow stage of the process by comparing the rates of each individual stage. The correct solution to this problem would allow us to outline a way of accelerating the slow stage, thereby making the whole process more efficient.

EXPERIMENTAL

The experimental procedures for the reaction of ethylenediamine and acetic acid (1:1.05 mole/mole) on Al_2O_3 have been described elsewhere [6]. The 2-MIn for dehydrogenation was used in both the molten state and in the form of a 70% aqueous solution. GLC analysis of the products has been described in [6].

Acetic acid (chemically pure grade) was used without further purification. Ethylenediamine was dried by heating it with KOH (residual water content 1.4%) and then fractionally distilling it. The 2-MIn was prepared by heating diacetylethylenediamine with CaO for 2 h at 210-220°C [8]. The pure product was separated by a two-stage fractional distillation (bp 195-200°C).

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Fig. 1. Effect of contact time (τ) on the product yield (Y) for the reaction between ethylenediamine and acetic acid in the presence of γ -Al₂O₃: 1) 2-methylimidazoline and 2-methylimidazoline; 2) monoacetylethylenediamine; 3) diacetylethylenediamine.

TABLE 1. Variation in the Yields of 2-Methylimidazoline and 2-Methylimidazole from Ethylenediamine and Acetic Acid in the Presence of γ -Al₂O₃ ($V = 1.2 \text{ h}^{-1}$, 400°C)

τ, h	Yield, mass %		
	2-MIn	2-MI1	Σ
0-2 2-4 4-6 6-8 8-10 10-12	80.9 81.2 88.9 88.8 89.2 89.5	6.7 6.8 3.5 3.0 3.3 2.0	87.6 88.0 92.4 91.8 92.5 91.5

The catalysts used were γ -Al₂O₃ type A-64 and the aluminoplatinum reforming catalyst AP-64k containing 0.6% Pt. The experiments were conducted at 330 and 400°C, the contact times being varied by altering the amounts of catalyst used.

RESULTS AND DISCUSSION

Formation of 2-Methylimidazoline. On passing a mixture of ethylenediamine and acetic acid through Al_2O_3 at 400°C a catalyzate was obtained containing a 2-MII as well as 2-MIn evidencing the presence of a certain number of dehydrogenating centers on the Al_2O_3 surface (Table 1). However, the dehydrogenating activity of Al_2O_3 falls quickly, accompanied by a reduction of 2-MII in the catalyzate. During this the total yield of 2-MII and 2-MIn does not decrease but actually increases somewhat.

The effect of the contact time (τ) on the yields of the main products was studied at 330 and 400°C. It can be seen from Fig. 1 that the total yield of 2-MIn and 2-MII increases sharply as τ increases and has already reached its maximum values (87-90%) at the shortest contact times even at 330°C. The only other products formed in appreciable amounts are mono- and diacetylethylenediamine (MAEDA and DAEDA). The MAEDA yield passes through a maximum as τ increases, which is characteristic of an intermediate compound (1). This maximum is higher at 330°C than at 400°C. Appreciable amounts of DAEDA are formed at 330°C and short τ . It is evident that under mild conditions the rate at which the second molecule of acetic acid is added to MAEDA becomes commensurate with the rate of cyclization of the latter to form 2-MIn. As T or τ



Fig. 2. Effect of contact time (τ) on the yield (Y) of 2-methylimidazole in the dehydrogenation of 2methylimidazoline in the molten state (1) and in aqueous solution (2) on AP-64k and on the total yield of 2methylimidazoline and 2-methylimidazole (3) from the reaction between ethylenediamine and acetic acid on γ -Al₂O₃. (•, values for the yields of 2-methylimidazole from the reaction between ethylenediamine and acetic acid on AP-64k).

Fig. 3. Effect of contact time (τ) on the yield (Y) of the main products of dehydrogenation of 2methylimidazoline (in aqueous solution) on AP-64K: 1) 2-methylimidazole; 2) unreacted 2-methylimidazoline; 3) 1-ethyl-2-methylimidazole; 4) monoacetylethylenediamine; 5) 1-ethyl-2-methylimidazoline.

increases, the cyclization process is accelerated to a greater extent and the DAEDA yield falls. It is also possible that under harsher conditions DAEDA is itself converted into 2-MIn, just as it is in the presence of other dehydrating agents [8].

Dehydrogenation of 2-Methylimidazoline. The dependence of the 2-MII yield on τ on the aluminoplatinum catalyst is illustrated in Fig. 2, where it can be seen that during conversion of molten 2-MIn the yields of 2-MII (curve 1) are significantly higher than those achieved at corresponding τ from mixtures of ethylenediamine and acetic acid. This could be explained by the fact that in the latter case water is formed along with the other products and this water retards the reaction. According to the stoichiometry 2 moles of water are formed for every mole of 2-MII. Therefore, in order to simulate this condition, when water vapor is present in the reaction zone a 70% aqueous solution of 2-MIn, in which its molar ratio to water is 1:2, is passed through the aluminoplatinum catalyst. In this case the curve for the dependence of the 2-MII yields on τ (curve 2) lies considerably below the yields obtained when the molten compound is used. It is significant that the points corresponding to the 2-MII yields obtained from ethylenediamine and acetic acid [6] coincide with the yields obtained when an aqueous solution of 2-MIn is used (curve 2). This agreement indicates that the rate-determining stage of the process is dehydrogenation of 2-MIn. This also follows from a comparison of the course of curve 2 with that of curve 3 (the variation in the 2-MIn yield from ethylenediamine and acetic acid on Al₂O₃). As can be seen, the 2-MIn yields increase more sharply with increasing τ than those of 2-MII pointing directly to the fact that the rate of formation of 2-MIn is faster than its dehydrogenation. During the dehydrogenation of 2-MIn in aqueous solution the same secondary products are formed along with the 2-MII as in the synthesis of 2-MII from ethylenediamine and acetic acid. These include: MAEDA, 1-ethyl-2-methylimidazole (1-E-2-MII), and 1-ethyl-2-methylimidazoline (1-E-2-MIn). MAEDA can be formed as a result of hydrolysis of 2-MIn by the water [9] that enters into the reaction zone with it. The MAEDA yield is highest at short τ and the lower temperature (Fig. 3). As τ and T increase the MAEDA yield falls sharply, which can be explained either by an increase in the fraction of 2-MIn entering into dehydrogenation, or by the possible involvement of MAEDA in some kind of further conversion. The formation of 1-E-2-MII and 1-E-2-MIn is not completely clear. These products were also detected earlier during the synthesis of 2-MII from ethylenediamine and acetic acid [6]. A scheme for their formation was put forward in which MAEDA was hydrogenated to N-ethylethylenediamine (N-EEDA), which then participated in a condensation reaction with a further molecule of acetic acid to form 1-E-2-MIn and 1-E-2-MII:

Partial hydrolysis to N-EEDA of the MAEDA produced during hydrolysis of 2-MIn cannot be ruled out in this case. However, this does not explain the appearance of 1-E-2-MII and 1-E-2-MIn since according to (2) another molecule of acetic acid is required for their formation. In addition, during dehydrogenation of molten 2-MIn in the absence of water MAEDA is not usually detected, but 1-E-2-MII is formed in considerable quantities. We can therefore assume that under the dehydrogenation conditions of 2-MIn partial hydrogenation of the imidazole ring or hydrocracking of N-EEDA also proceeds along with the main process. The C_2 fragments formed during this probably alkylate the nitrogen of 2-MII and 2-MIn.

Thus the catalytic synthesis of 2-MII is a complicated chain of successive and concurrent conversions that take place on different active centers and at different rates. At higher temperatures (370-400°C) the contribution of secondary processes is not significant and the main reaction proceeds with maximum selectivity.

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