The mechanisms of the formation of by-products in the catalytic synthesis of C-alkylimidazoles from diamines and carboxylic acids

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The formation of 1-ethyl-2-methylimidazole (1-Et-2-MI) and 1-ethyl-2-methylimidazoline (1-Et-2-MIN), intermediates in the synthesis of 2-methylimidazole (2-MI) from ethylenediamine (EDA) and AcOH in the presence of a platinum-on-alumina catalyst, was studied. Using $CH_3^{14}COOH$ the incorporation of two acetate units into 1-Et-2-MI and 1-Et-2-MIN molecules was demonstrated. The same products were also obtained on dehydrogenation of 2-methylimidazoline (2-MIN) under mild conditions (220–230 °C). A part of the latter is transformed to N-ethyl ethylendiamine (EEDA) and EDA. These facts indicate that both 1-Et-2-MI and 1-Et-2-MIN result from hydrogenolysis of the imidazoline ring with subsequent ethylation. A reverse reaction, the C₅-cyclization of EEDA, was also observed. The formation of 2-MI is favored by increasing temperature.

Key words: C-alkylimidazoles; platinum-on-alumina catalyst; 1-ethyl-2-methylimidazole; 1-ethyl-2-methylimidazoline.

The main by-products in the catalytic synthesis of 2-methylimidazole (2-MI) from ethylenediamine (EDA) and acetic acid in the presence of a bifunctional platinum-on-alumina catalyst¹ are 1-ethyl-2-methylimidazole (1-Et-2-MI) and 1-ethyl-2-methylimidazoline (1-Et-2-MIN). It has been suggested¹ that monoacetyl ethylenediamine (MAEDA), the intermediate in this process, is reduced to N-ethyl ethylenediamine (EEDA) and the latter interacts with the second molecule of AcOH to give the aforementioned products (Scheme 1).

Scheme 1

However, the possibility of N-alkylation of 2-MI and 2-MIN by ethylene, which probably appears as a result of deamination of EDA and is usually present in the end gases, can not be ruled out. Other considerations² about the mechanisms of formation of 1-Et-2-MI were put forward in a study of dehydrogenation of 2-methylimidazoline (2-MIN). 1-Et-2-MI and 1-Et-2-MIN were also found among the reaction products, although neither EDA nor acetic acid were used in the reaction (Scheme 2). In this case EEDA was also suggested to be an intermediate.

However, if, according to Scheme 1, the transient EEDA is formed on the reduction of its precursor,



Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 5, pp. 937-940, May, 1993. 1066-5285/93/4205-0895 \$12.50 © 1994 Plenum Publishing Corporation MAEDA, and then undergoes intermolecular acylation followed by heterocyclization and subsequent dehydrogenation to give 1-Et-2-MIN and 1-Et-2-MI, respectively, then according to Scheme 2 it results from the reductive cleavage of the pre-formed 2-MIN. Then EEDA formed by the second mechanism alkylates the nitrogen atom in 2-MI and 2-MIN. This process gives rise to the elimination of EDA and the formation of 1-Et-2-MI or 1-Et-2-MIN, respectively.

The present paper is devoted to the solution of the problem of the genesis and mechanisms of formation of these products. In order to find the source of carbon in the ethyl radical of 1-Et-2-MI, the transformations of a mixture of EDA with acetic acid labeled with 14 C were studied.

Experimental

Catalytic experiments were carried out using a flow setup which was loaded with 1–17 cm³ of the reforming catalyst, AP-64K (0.6 % Pt/Al₂O₃). The reactants were introduced through a calibrated hot feeder which made it possible to pass liquid products and melts at temperatures up to 120 °C. Equimolar mixture of EDA and MeCOOH, 2-MIN, EEDA, and an ethanol solution of 2-MI were used separately as starting compounds. The duration of the experiments was 1–2 h at 220–400 °C. The volume rate of feeding of the starting compounds (ω) was 0.6 h⁻¹. Each of the four starting compounds was diluted with hydrogen or nitrogen in the ratio H₂ (N₂): substrate = 4 : 1 (mol/mol).

The analysis of the products was carried out chromatographically on a column (2.5 m × 4 mm) packed with 5 % polyethylene glycol 20M on Inerton impregnated with a 0.9 % KOH solution. The analyses were made at 175 °C with subsequent heating to 200 °C; the rate of the carrier gas (He) was 30 cm³ min⁻¹. For the separation of EDA and EEDA another column (1.5 m × 4) mm, filled with Polysorb-1, was used (230 °C, He rate 50 cm³ min⁻¹).

The experiments with a mixture of EDA and Me¹⁴COOH were performed under conditions similar to those descibed above for the non-labelled compounds, but their duration was only 20 min. In this case, during the GLC analysis of the reaction mixture, the outlet of the katharometer was connected with a U-shaped tube filled with CuO and placed into an oven (600 °C). Here the components of the mixture emerging from the column were burnt; the water vapor thus formed was separated using a trap, and the remaining CO₂ was directed to a flow counter of radioactivity. Thus, in parallel with the concentrational chromatogram, a radiochromatogram was recorded, which made it possible to determine the molar radioactivity (MRA) for each component of the mixture. The values of MRA were expressed in relative units, the molar radioactivity of 2-methylimidozole being taken as unity.

Commercial EDA was desiccated by heating with granulated KOH, and distilled. EEDA was prepared by alkylating EDA with ethyl chloride according to the procedure described in ref. 3. 2-MIN was obtained from diacetylethylenediamine (DAEDA) by heating it with CaO according to the reported procedure,⁴ and purified by repeated distillation of the product. Acetic acid of "chemically pure" grade was used without additional purification.

Table 1. Molar radioactivity of the main products of interaction of ethylenediamine with acetic acid (AP-64K catalyst, H_2 : EDA = 4 : 1)

Reaction	conditions	Molar radioactivity (rel. units)					
<i>T</i> ∕°C	ω/h ⁻¹	2-MIN	I-Et-2-MI	2-MI			
300	0.68	_	2.08	1			
			2.29	1			
			1.90	1			
			2.34	1			
			2.15*	1*			
330	2.76	1.14	2.02	1			
		0.95	1.91	1			
		1.06	2.03	1			
		1.25	2.40	1			
		1.10*	2.10*	1*			

*Average value.

Results and Discussion

In experiments with ¹⁴C-labelled acetic acid, the MRA of the main reaction products were determined. It was found that the MRA of 1-Et-2-MI was twice as high as those of the non-alkylated products, 2-MI and 2-MIN (Table 1). This fact rules out the assumption that the products of EDA deamination participate in the alkylation of 2-MI and implies that the acetic acid carbon atom takes part in the formation of the ethyl group in 1-Et-2-MI.

In order to explain the transition of the ¹⁴C-atom from acetic acid to the ethyl group, the dependence of the formation of 1-Et-2-MI on the reaction conditions and the nature of the carrier gas was studied, as well as the transformations of possible intermediates in the synthesis of 2-MI. As can be seen from Table 2, the content of 1-Et-2-MI in the reaction mixture did not exceed 0.5 % (run 1) under the optimum conditions of the process (400 °C, $\omega = 0.66 \text{ h}^{-1}$, H₂ : EDA = 4 : 1); the concentration of this product increased to 22.7 % only when the reaction temperature was reduced to 300 °C (run 2). It should be noted that substituting nitrogen for hydrogen (run 5) dramatically decreased the yield of 1-Et-2-MI (from 22.7 % to 0.1 %). Thus, the elimination of the hydrogenating agent from the reaction zone resulted in the nearly complete suppression of the formation of N-substituted 2-methylimidazole. The yield of this product decreased also when the fraction of acetic acid in the starting mixture was reduced (runs 2-4). These results and the results of the experiments with Me¹⁴COOH are in agreement with the mechanism shown on Scheme 1.

However, these results do not contradict the formation of 1-Et-2-MI according to Scheme 2. In fact, the acetate fragments can participate twice if the Me-C fragment is transferred first from 2-MIN to EEDA

Run	Molar ratio	Reaction		Composition of the product mixtures ^a (mass. %)							
	of reactants	T/°C	ω/h ⁻¹	Light products	1-Et-2-MIN	2-MIN	l-Et-2-MI	MAEDA	DAEDA	2-MI	
1	EDA : MeCOOH = 1 : 1.17	400	0.64				0.5			95.5	
2	EDA : MeCOOH = 1 : 1.7	300	0.64	3.0	0.3	0.6	22.7		0.4	69.9	
3	EDA : MeCOOH = 1:1	300	0.64	7.7	0.7	12.9	9.9	2.4	0.7	60.9	
4	EDA : MeCOOH = 1.32 : 1	300	0.64	14.2	1.4	37.9	3.0	1.4	0.4	38.0	
5 ^b	EDA : MeCOOH = 1 : 1.17	300	0.64	0.4	0.1	17.2	0.1	0.5	0.4	80.8	
6°	2MI : EtOH = 1 : 3	350	0.66	15.5	_	—	62.2				
7	EEDA	300	0.64	14.5		1.1	58.3			25.4	

Table 2. The formation of 1-Et-2-MI from different starting compounds (the AP-64K catalyst, molar ratio H_2 : EDA = 4 : 1)

^aThe balance (to 100 %) are 1,2-dimethylimidazole, condensation products, and unidentified compounds. ${}^{b}N_{2}$: EDA = 4 : 1. ${}^{c}Al_{2}O_{3}$ as the catalyst. The experiment was carried out without any carrier gas.

during hydrogenolysis and then to the nitrogen atom of another molecule of 2-MI or 2-MIN. The above-mentioned beneficial effect of hydrogen on the formation of 1-Et-2-MI can manifest itself not only in the reduction of the C=O group in MAEDA (see Scheme 1) but also in the hydrogenolysis of the imidazoline cycle to EEDA. Thus, when a mixture of EDA and acetic acid was diluted with nitrogen (see Table 2, run 5), 1-Et-2-MI was practically absent in the reaction products, whereas the content of 2-MIN increased sharply (to 17 %). This is not surprising because in this case the latter was not consumed in the formation of EEDA or, consequently, 1-Et-2-MI.

It was necessary to examine the formation of 1-Et-2-MI in more detail. Therefore, in order to detect EEDA among the reaction products, we studied the transformations of 2-MIN at temperatures as low as possible (200-220 °C) and we studied the temperature dependence of the yield of EEDA. Moreover, the feasibility of alkylating 2-MI at the N atom by EEDA and EtOH in the presence of the platinum-on-alumina catalyst or Al₂O₃ alone was also examined.

In fact, EEDA and EDA have been found among the transformation products of 2-MIN in the presence of the platinum-on-alumina catalyst, whereas C_2H_6 was

found in the gas phase. The largest amounts of these products (Table 3) were formed at 220-230 °C. Their content decreased as the reaction temperature increased, which can probably be explained by the involvement of these products in further transformations. (For example, the N-alkylation of 2-methylimidazole or dehydrodeamination leading to pyrazine or methylpyrazine;⁵ the latter two were detected by mass-spectroscopy among the decomposition products of 2-MIN.)

The possibility of the addition of an ethyl group to the N atom of imidazole was confirmed by direct experiments. On passing an equimolar mixture of 2-MI with EEDA over the catalyst at 300 °C, the formation of up to 47 % of 1-Et-2-MI was observed. The same product (up to 62 %) was also obtained by passing an ethanolic solution of 2-MI through Al_2O_3 (see Table 2, run 6). Interestingly, 1-Et-2-MI, 2-MI, and 2-MIN were formed from EEDA even in the absence of 2-MI (see Table 2, run 7). Consequently, not only the opening of the imidazoline ring but also the reverse reaction, cycle formation, took place. It seems likely that this C₅cyclization of EEDA proceeds with the intermediate formation of imines and diimines, that is, by stepwise dehydrogenation, as it is known for C₅- and C₆cyclization of hydrocarbons.⁶ Partial deethylation of

Table 3. The transformations of 2-MIN in the presence of the platinum-on-alumina catalyst with a uniform increase in temperature ($\omega = 0.66 \text{ h}^{-1}$, H₂: 2-MIN = 4 : 1)

<i>T</i> /° <i>C</i>	Catalysate composition* (mass. %)										
	Decom- position products	EDA	EEDA	1-Et-2-MIN	2-MIN	1,2-DMI	1-Et-2-MI	MAEDA	2-MI	The sum of imida- zoles	The sum of N-substituted imidazoles and imidazolines
220-230	1.8	7.8	6.6	9.7	59.0	1.4	0.8	2.2	6.7	89	11.9
230-250	2.3	5.1	6.8	5.0	59.1	1.2	0.8	7.0	6.5	8.5	70
250-270	2.9	4.8	4.4	3.0	58.2	1.1	1.3	9.4	6.7	9.1	54
270-290	3.3	4.9	2.6	2.8	54.4	0.9	1.6	7.9	12.6	15.1	5.3
290-315	2.4	4.6	1.5	1.4	34.4	0.5	5.8	9.7	31.1	37.4	7.7

* The balance (to 100 %) are unidentified compounds.



 $H_2NCH_2 - CH_2NH_2 + C_2H_4$

EEDA was also observed, since up to 3 % of the C_2 -hydrocarbons were found in the gas phase. Taken together, all these facts make it possible to propose a general scheme for the transformations occurring during the preparation of 2-MI from EDA and MeCOOH in the presence of the platinum-on-alumina catalyst (Scheme 3).

The formation of EEDA by direct hydrogenation of MAEDA is not very probable because, according to the literature data,⁷ the reduction of amides occurs with great difficulty and requires enhanced pressures (3-4 MPa). Intermolecular dehydrogenation with subsequent hydrogenolysis is energetically more favorable, and this is directly confirmed by the experiments. It should be noted that the formation of EEDA and the subsequent alkylation of 2-MI and 2-MIN occur to the largest extent at low temperatures (below 300 °C), and already at 370-400 °C the rate of dehydrogenization of 2-MIN becomes sufficient to reduce the yield of 1-Et-2-MI. Moreover, at higher temperatures the process of dealkylation begins to appear. Thus, the increase in temperature not only brings about an increase in the yield of 2-MI, but also suppresses the side reaction of 1-Et-2-MI formation, which results in better selectivity of the process.

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