ELECTROCHEMICAL OXIDATION OF 2-AMINOBENZIMIDAZOLE IN THE PRESENCE OF ADDITIVES

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Summary

We studied the oxidation of 2-aminobenzimidazole in acetonitrile on a Pt anode in the presence of additives (collidine, pyridine, diethyl malonate, perchloric acid, anhydrous sodium carbonate) by cyclic voltammetry. At the potentials determined in these experiments we studied anodic oxidation processes. We stated that the additives largely influence anodic oxidation: the time for controlled-potential electrolysis is reduced, the chemical reaction following electron transfer is accelerated and the process mechanisms change. Basic additives (collidine, pyridine, sodium carbonate) promote formation of oligomers deposited on the electrode surface, while nucleophilic additives reduce their amount and make nucleophilic substitution possible. With an additive both basic and nucleophilic (pyridine), only its basic effect promoting deprotonation manifests itself; a basic, but not nucleophilic additive (collidine) contributes both to the proton transfer step of the 2-aminobenzimidazole cation radical and to its deprotonation; in the process, a product is formed that does not appear in the absence of additive.

In our previous paper [1] we reported results of studies by cyclic voltammetry and controlled-potential electrolysis of the electrochemical oxidation of 2-aminobenzimidazole (AB) in acetonitrile, using a platinum electrode. We also outlined the likely mechanism of the process.

It is known that to study and carry out oxidative or reductive electrode processes, additives are frequently utilized, to trap reactive intermediates, to change the mechanism of the electrode process and to confirm individual steps of the assumed mechanism [2]. To confirm proton transfer steps of anodic processes, collidine is most universally in use [3, 4]: to trap imminium cations, collidine is applied together with diethyl malonate [5] and to confirm the protonation character of the products of the electrode process, perchloric acid and anhydrous sodium carbonate are usually utilized [6]. Pyridine has been successfully used as a proton trap promoting anodic oxidation without participating in the electrode process [7].

In this paper we report on cyclic voltammetry and controlled-potential electrolysis of AB in the presence of nucleophilic, basic, but not nucleophilic as well as acidic additives. Our purpose was to confirm individual steps of the reaction mechanism proposed earlier [1], to accelerate the electrode processes

and to study the feasibility of producing new compounds. Additives appeared of importance, since in their absence—by reason of the poor conductivity of the oligomers deposited on the surface of the anode—anodic oxidation of AB proceeds rather slowly.

Experimental

The materials, instruments and methods used in our experiments were described in detail in our previous paper [1].

The additives used were: 2,4,6-collidine (collidine), diethyl malonate, perchloric acid 70%, pyridine and anhydrous sodium carbonate. All were analytical-grade reagents REANAL.

Results and discussion

By studying the effect of electroinactive, basic, but not nucleophilic collidine on the cyclic voltammetric curve (CV) of AB we were able to confirm that a proton transfer step follows electron transfer.

Figure 1 shows the voltammetric curves of AB alone and in the presence of various amounts of collidine. The curves were taken in acetonitrile solution containing 0.1 mol tetrabutylammonium perchlorate (TBAP) as supporting electrolyte, using a platinum spot electrode and a scan-rate of 400 mV/s. Figure 2 represents anodic peak current *versus* molar ratio collidine/AB.

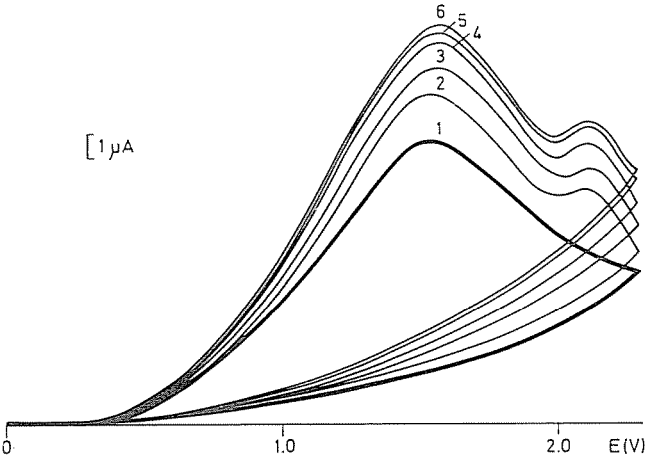

Fig. 1. Cyclic voltammetric curves of 2-aminobenzimidazole (1) and of 2-aminobenzimidazole in the presence of increasing amounts of collidine (2–6)

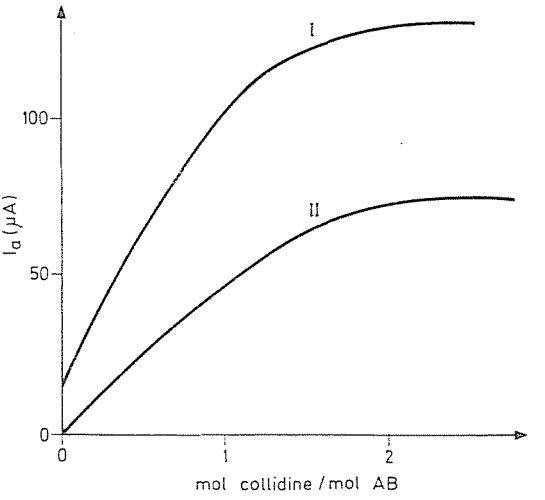

Fig. 2. Anodic peak currents *vs.* molar ratio of 2-aminobenzimidazole to collidine
I — first anodic peak current, II — second anodic peak current

The figures clearly indicate that proton transfer has a decisive role in the electrode process corresponding to the first peak potential in cyclic voltammetry. The current of the first peak increases substantially under the effect of collidine, and the second cyclic voltammetric peak—which, without collidine, does not appear at the scan rate of 400 mV/s—also manifests itself and its current increases with increasing amount of collidine.

The effect of nucleophil, basic pyridine on the CV curves is represented in Fig. 3, demonstrating that the first wave did not change by the presence of

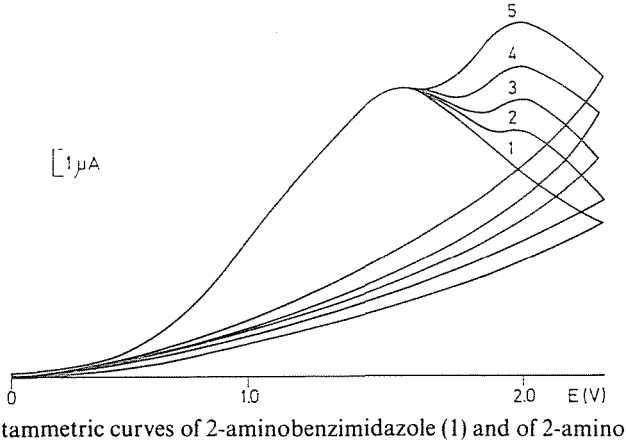

Fig. 3. Cyclic voltammetric curves of 2-aminobenzimidazole (1) and of 2-aminobenzimidazol in the presence of increasing amounts of pyridine (2–5)

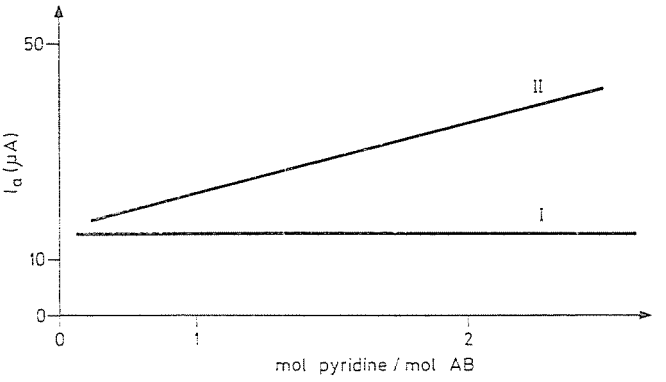

Fig. 4. Anodic peak currents *vs.* molar ratio of 2-aminobenzimidazole to pyridine
I — first anodic peak current, II — second anodic peak current

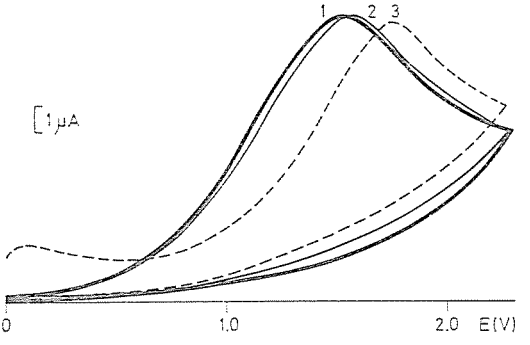

Fig. 5. Cyclic voltammetric curves of 2-aminobenzimidazole (1) and of 2-aminobenzimidazole in the presence of 0.1 mol diethyl malonate (2) and of 1 mol diethyl malonate (3)

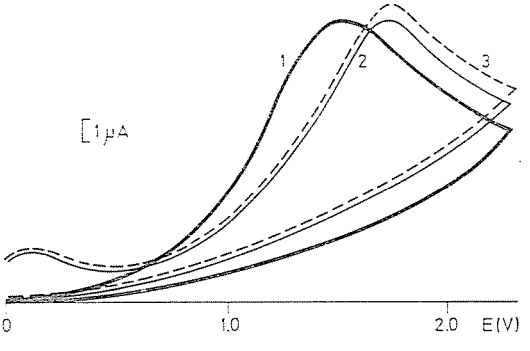

Fig. 6. Cyclic voltammetric curves of 2-aminobenzimidazole (1) and of 2-aminobenzimidazole in the presence of 1 mol diethyl malonate (2) and of 1 mol diethyl malonate and 1 mol collidine (3)

pyridine, but the second wave appeared more expressly and its current increased to a greater extent with increasing pyridine concentration than in the presence of collidine. Within the pyridine concentration range applied, no steady state was established, as demonstrated by the curves of peak current *versus* molar ratio pyridine to AB (Fig. 4).

The above results indicate that the electrode process presumably proceeds in another direction by the action of the nucleophil base. Figs 3 and 4 also evidence that controlled-potential electrolysis performed at the first CV peak potential will not lead to the formation of anodically pyridinated compounds. The basic character of pyridine presumably affects the electrode process to a greater extent than its nucleophilicity.

The effect of neutral and nucleophil diethyl malonate on the cyclic voltammetry curve of AB is represented in Fig. 5, indicating that addition of small amounts (0.1 mol) of diethyl malonate does not noticeably change the CV curve of AB. As soon, however, as the molar ratio of diethyl malonate to AB reaches 1 : 1, the first peak potential is shifted by 200 mV in the anodic direction, without an increase in the peak current; at a potential of 0.15 V another anodic wave also appeared on the curve. The changes effected by the additive on the CV curve are presumably due to the action of the additive on the chemical reaction following the electron transfer.

The joint effect of diethyl malonate and collidine on the CV curve of AB is shown in Fig. 6. The figure clearly demonstrates that the anodic peak potential shifted by the effect of diethyl malonate addition, and the current increases in the presence of collidine. The increase of the peak current, however, is less than in the system not containing diethyl malonate. Similarly to the CV curves taken in the presence of pyridine, it is the effect of the basic collidine promoting proton transfer that manifests itself.

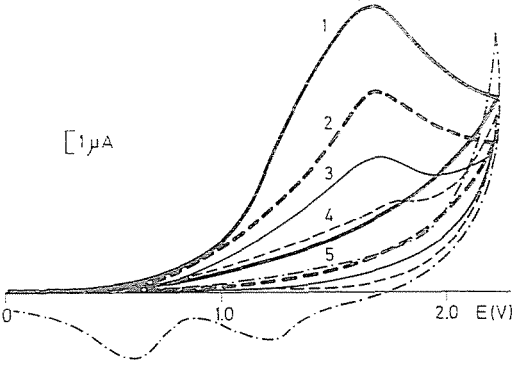

Fig. 7. Cyclic voltammetric curves of 2-aminobenzimidazole (1) and of 2-aminobenzimidazol in the presence of 0.02 mol perchloric acid (2), of 0.1 mol perchloric acid (3), of 0.2 mol perchloric acid (4) and of 0.2 mol perchloric acid + sodium carbonate in excess (5)

Addition of perchloric acid results in a gradual decrease of the peak current; at 0.2 mol the peak disappears completely. Addition of anhydrous sodium carbonate does not result in the reappearance of the peak; however, two cathodic peaks, not observed in the previous experiments, appear at 0.52 and 1.15 V potential values (Fig. 7). The latter is presumably the cathodic peak corresponding to the first anodic peak of AB. From this result one may conclude that protonation of AB is irreversible.

Controlled-potential electrolyses

Controlled-potential electrolyses (CPE) were performed with the technique and conditions reported in our earlier paper [1] at two peak potentials (1.52 and 1.98 V) of the CV curve of AB in the presence of additives. The molar ratios of AB to additive applied were 2 : 1.

CPE in the presence of collidine proceeded rapidly at both potentials. During electrolysis at 1.52 V, the value of the current decreased from the initial 80 mA after 1 F/mol electricity consumed, whereas in the process controlled at the second peak potential, i.e. 1.98 V, the current, from the initial 160 mA, did not fall below 40 mA even after 2 F/mol electricity consumed. The colour of the anolyte changed in both cases from dark violet over yellow to dark brown, and the surface of the electrode became coated with a thick, dark brown layer consisting presumably of oligomers. The violet colour of the solution is attributable to the presence of the cation radicals formed in the first step; these radicals then participate in further reactions, as also indicated by the colour change of the solution.

Thin-layer chromatography of the anolyte [1] indicated that product distribution was identical in the processes performed at both potentials, although at 1.52 V the amount of electricity consumed was exactly 1 F/mol, whereas at 1.98 V the electrode process was not completed even after 2 F/mol. From the anolyte we succeeded to isolate, in both cases, a product with $R_f = 0.71$ (the R_f value of AB is 0.22); its yield was around 20%, its mass number as determined by mass spectrometry was 169. The isolated product should be considered the main product, despite the fact that a relatively heavy coating (about 25—45%) was deposited on the surface of the electrode, and the unreacted starting material made out at least 20%. NMR investigation of the electrolysis product with the mass number 169 indicated that it is a hydrated product formed by splitting of the imidazole ring.

Thus, collidine, by its basic nature, promoted deprotonation of the cation radical, and the proton transfer process; it accelerated the reaction compared to the reaction proceeding without additive. Since deprotonation of the cation radicals leads to the formation of free radicals, it is comprehensible that the

amount of oligomers deposited on the electrode surface increased in the presence of collidine. The product with the mass number 169 formed in the electrolyte solution may be attributed to the cation radicals not only being subjected to deprotonation, but also—by proton transfer and disproportionation—to transformation into dications. The further reaction of the dications might then lead to the above product.

Since the current of the first anodic peak of the CV curve did not increase in the presence of pyridine, we performed preparative anodic oxidation only at the second anodic peak potential.

In the presence of the nucleophilic base pyridine, we found that the rate of the electrode process increased largely, and so did the amount of deposits on the electrode surface. It is of interest that electrolysis current—even after the consumption of 2 F/mol of electricity—decreased very slightly only as compared to the initial current. This finding is very probably related to the formation of the electroconductive coating on the electrode surface.

After completion of electrolysis the amount of the coating was about 70% of the amount of starting material, and unreacted AB could be estimated by thin-layer chromatography to 20%. Besides AB, only impurities could be detected in the electrolyte solution.

Consequently, pyridine participated in the electrochemical oxidation process of AB only as a base and not as nucleophilic additive, and for this reason no anodic substitution of pyridine took place. The presence of basic pyridine accelerated deprotonation of the cation radicals to an extent that no dications could be formed, and the formation of oligomers by the radical mechanism came to the fore.

CPE in the presence of nucleophilic, but not basic diethyl malonate proceeded rapidly at both potential values, but the amount of oligomers deposited on the electrode surface was negligible. After the one-electron process performed at 1.52 V, we succeeded to isolate a stable product from the electrolyte, with an R_f value of 0.52 (the R_f value of AB was 0.11). The product was poorly soluble in organic solvents. Its IR spectrum indicated that AB had reacted with diethyl malonate, that is, anodic substitution had taken place. The exact structure of the product could not, however, be determined, owing to its limited solubility.

We then performed CPE at the first CV peak potential (1.52 V) in the joint presence of collidine and diethyl malonate, hoping that in this manner the advantages of both additivies could be combined. However, except oligomers deposited on the electrode surface, only formation of unstable products could be observed in the electrolyte.

Although CV studies indicated that anhydrous sodium carbonate does not affect the electrode process, we also performed CPE in the presence of this additive insoluble in the system in question. The results were similar to those

obtained with pyridine: the insoluble base sodium carbonate also accelerated deprotonation and thereby promoted the formation of the products by the radical mechanism.

One may conclude that by using additives, time required for CPE can indeed be reduced. Basic additives (collidine, pyridine, sodium carbonate) favour formation of oligomers deposited on the electrode, whereas nucleophil additives (diethyl malonate) reduce their amount and give rise to nucleophilic substitution.

In order to produce stable products, application of collidine and diethyl malonate, resp., seems suitable. In the presence of these additives products were formed that do not form without additive. These additives hence change the mechanism of the process and allow to produce new compounds.

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