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## ELECTROCHEMICAL BEHAVIOUR OF 1-(o-NITROBENZYLIDENE)AMINO-4,6-DIPHENYL-2-PYRIDONE

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### ABSTRACT.

The electrochemical behaviour of 1(o-nitrobenzylidene)amino-4,6-diphenyl-2-pyridone, in ethanolic Britton-Robinson buffer, has been studied using polarographic, voltammetric and controlled-potential electrolysis methods.

Reduction of -NO<sub>2</sub> group to -NHOH is first observed in acidic and neutral media, while reduction of the aldiminic bond (similarly as it takes place in analogous compounds), accompanied by hydroxylamine reduction, occurs later. In basic medium, reduction of hydroxylamine is easier than that of the aldiminic bond.

The hydroxylamine stability is pH dependent, it is stable in neutral medium and unstable in acidic and basic media. As a consequence, the appearance of an ECE mechanism --in the reduction of -NO<sub>2</sub> group-- is observed in basic medium.

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## INTRODUCTION.

The aldimines derived from 1-amino-4,6-diphenyl-2-pyridone are of great interest in organic synthesis, because they allow the transformation of aldehydes to nitriles (1,2) and phenacyl bromides to aroyl cyanides (3). Also these aldimines have a large electrochemical activity, giving one or two reduction waves which yield 4,6-diphenyl-2-pyridone and a benzylamine, with the benzylimine as intermediate, through a transfer of four electrons (4). This reduction mechanism suggests a new utilization of these compounds: in fact, as the synthesis is made through the condensation of an aldehyde with 1-amino-4,6-diphenyl-2-pyridone, these aldimines could be utilized as intermediates for the transformation of aldehydes to amines.

In this paper we approach the study of 1-(o-nitrobenzylidene)amino-4,6-diphenyl-2-pyridone using dc polarography, cyclic voltammetry and controlled-potential electrolysis. This compound differs from other aldimines by the presence of an easily reducible  $-\text{NO}_2$  group in such a position that its reduction intermediates can interact with the aldiminic bond.

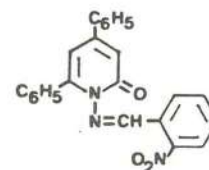
## EXPERIMENTAL.

## Apparatus.

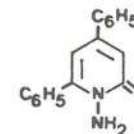
Dc polarograms were recorded on an AMEL 471 multipolarograph with a three electrode system, using a thermostated cell ( $25 \pm 0.1^\circ\text{C}$ ). Potentials were referred to the SCE. The capillary used had the following characteristics when immersed in a Britton-Robinson buffer containing 60% (vol.) ethanol ( $\text{pH} = 10.7$ ), at  $h = 55$  cm and  $-1.5$  V:  $m = 1.09$  mg/s and  $t = 5.98$  s. Voltammetric studies were carried out using an AMEL 448 oscilloscope with an HMDE working electrode, area  $1.3 \text{ mm}^2$ . Coulometric determinations of the electrons involved and preparative macroelectrolysis were made in an AMEL 551 potentiostat with an AMEL 563 integrator and an HP-AMEL 862/D recorder. In both cases a mercury pool electrode (area =  $7 \text{ cm}^2$ ) was used, stirred by a magnetic stirrer. The IR spectra were obtained in a Perkin-Elmer 257 spectrophotometer. The pH values were measured with a Philips pH-meter, Model pw 9408.

## Chemicals.

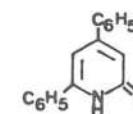
1-(o-nitrobenzylidene)amino-4,6-diphenyl-2-pyridone (I) (mp  $156^\circ\text{C}$ , lit.  $156^\circ\text{C}$ ) was prepared by condensation of 1-amino-4,6-diphenyl-2-pyridone and o-nitrobenzaldehyde (2). 1-amino-4,6-diphenyl-2-pyridone (II) (mp  $166^\circ\text{C}$ , lit.  $166^\circ\text{C}$ ) and 4,6-diphenyl-2-pyridone (III) (mp  $208^\circ\text{C}$ , lit.  $204\text{--}208^\circ\text{C}$ ) were prepared by condensation of 4,6-diphenyl-2-pyridone and hydrazine (5) and cyclization of benzoylacetonitrile with acetophenone by polyphosphoric acid (6) respectively.



(I)



(II)



(III)

All compounds (I - III) were recrystallized from ethanol and were chromatographically homogeneous. All other chemicals were of Merck reagent grade and their solutions were prepared in twice distilled water. Mercury was first electrolytically purified and distilled three times.

## Procedures.

To increase solubility and hold constant buffer capacity in presence of 60% ethanol, a Britton-Robinson buffer was prepared using a mixture of 0.4 M acetic, phosphoric and boric acids to which 2 M potassium hydroxide (rather than sodium hydroxide) was added. Final concentration of the acids was 0.016 M. The ionic strength was held constant at 0.1 M by addition of potassium chloride (7). A  $1.10^{-2}$  M stock solution of compound (I) was added to a final concentration of  $1.10^{-4}$  M in the buffered solutions, and the 60% (vol.) ethanolic solution was purged by nitrogen for 20 minutes.

The potential selected for controlled-potential electrolysis corresponded to the crest of the polarographic wave. Coulometric measurements were conducted with  $1.0 - 2.0 \cdot 10^{-4}$  M solutions. The cell was



flushed continuously with nitrogen and the electrolysis was continued until the current had decayed to the background level. Completion of the electrolysis was confirmed by polarographic measurements. The same procedure was used in macroscale electrolysis except that solutions were  $1 - 2 \cdot 10^{-3}$  M in the compound studied. The identification of 4,6-diphenyl-2-pyridone and 1-amino-4,6-diphenyl-2-pyridone among electrolysis products was made as follows: ethanol was separated from the electrolysed solutions by distillation at reduced pressure, precipitating white solids of mp  $210^\circ\text{C}$  and  $166^\circ\text{C}$  respectively, whose IR spectra were just the same than the ones of authentic samples of 4,6-diphenyl-2-pyridone and 1-amino-4,6-diphenyl-2-pyridone, and in agreement with reports in the literature (5, 6).

The values  $n$  were computed from the slope of plots of  $E$  vs  $\log \bar{I}/(\bar{I}_d - \bar{I})$ . To construct these plots special polarograms were recorded with a very slow rate of scanning (0.5 mV/s).

#### RESULTS AND DISCUSSION.

##### dc polarography.

The reduction of 1(o-nitrobenzylidene)amino-4,6-diphenyl-2-pyridone in our experimental media (ethanolic buffered solutions) shows two or three polarographic waves. In acidic and neutral media two waves are obtained, A and B, while in basic medium the wave A is gradually transformed into a third wave A', although the wave A does not disappear completely (Fig. 1). By the comparison of these waves with those of similar compounds (4) we can assign the wave B to the nitro group reduction.

From the influence of the concentration of aldimine, mercury pressure, dropping time and temperature on the polarographic waves, is established that all the waves are diffusion controlled, except B in basic medium. In this case we have observed some kinetic character through several facts as: non-linear plots of  $\log \bar{I}_l$  vs  $\log t_d$ , smaller dependence of intensity with mercury pressure than in a diffusion process, and a high enough temperature coefficient (greater than  $3\%/^\circ\text{C}$ ). In addition, taking into account the dependence of  $\bar{I}_l$  on pH (Fig. 2), we can conclude that the partial kinetic character is due to an ECE mechanism, in which the rate of the chemical reaction is increased with

pH. The product of this chemical reaction is easier reducible than nitroaldimine and, so, only one polarographic wave appears.

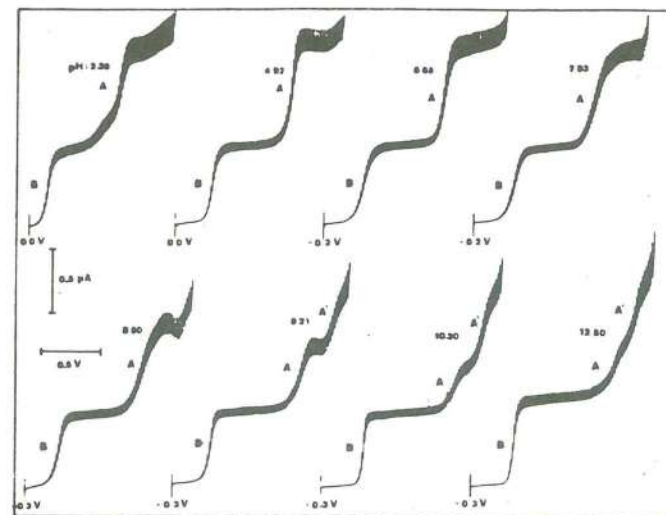


Figure 1.

pH-dependence of the polarographic waves of 1-(o-nitrobenzylidene)amino-4,6-diphenyl-2-pyridone. 60 % (vol.) ethanolic Britton-Robinson buffer,  $1 \cdot 10^{-4}$  M aldimine, 0.001 Triton X - 100. The pH values of solutions are indicated on each curve. Drop time: 3 s.

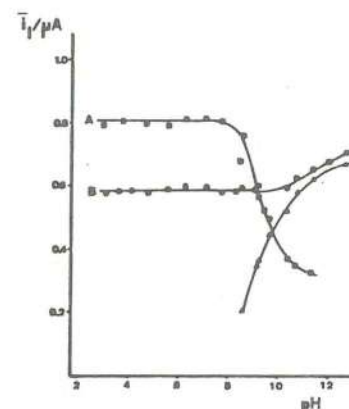


Figure 2.

pH-dependence of limiting currents of aldimine. (a) wave A; (b) wave A'; (c) wave B. Conditions as in figure 1.

Studying the dependence of the half-wave potential of A with pH we can obtain a value of  $pK = 7.2$  for this compound, and the corresponding value of  $pK' = 9.7$ , is the same as that found from the plot of  $\bar{I}_l$  vs pH (Fig. 3). Likewise, from the dependence of the half-wave potential and the intensity of the waves on pH (Figs. 2 and 3, Table I), and similarly to other aldimines, is deduced that wave A is due to the reduction of diprotonated aldimine. Usually, these aldimines present two centers of basicity --the aldiminic

nitrogen and the carbonyl oxygen (4,8,9)-- on which the first protonation can take place. If we admit that wave B is due to the reduction of  $-\text{NO}_2$  to  $-\text{NHOH}$ , it would be necessary to consider one other possible tautomeric form: that one which holds protonation in the hydroxylaminic oxygen. However, taking account the similarity of the wave A with the corresponding ones of other aldimines, we can affirm that, on the electrode surface, this tautomeric form is not of great importance. This would not be so if the hydroxylaminealdimine had existence in the bulk of the solution, for the hydroxylaminic oxygen must hold a very similar basicity, or perhaps less than the hydroxylaminic one, because the different hybridization of both ( $\text{sp}^2$  and  $\text{sp}^3$ ), while the aldiminic nitrogen has an important steric hinderance. Similarly, we consider that, in the electrode surface, the diprotonated form would lodge the protons on the carbonyl oxygen and on the aldiminic nitrogen.

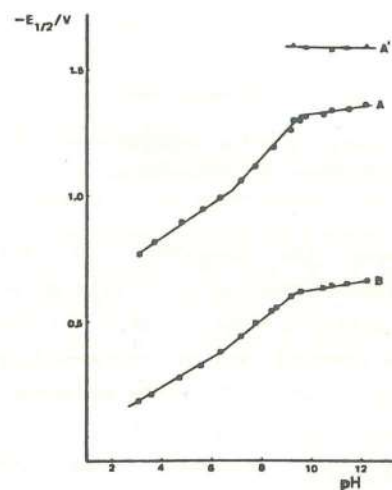


Figure 3.  
pH-dependence of half-wave potentials of individual waves of 1-(o-nitrobenzylidene)amino-4, 6-diphenyl-2-pyridone.  
Conditions as in figure 1.

TABLE I  
Polarographic data obtained for the reduction of 1-(o-nitrobenzylidene) amino-4,6-diphenyl-2-pyridone  $1.10^{-4}$  M in 50 % ethanolic Britton Robinson Buffer, 0.001 % Triton X - 100. Drop time: 3 s.

pH range	wave	$\frac{dE_{1/2}}{dpH}$	$\Delta$ (*)
4.5 - 6.5	A	0.068	0.062
4.5 - 6.5	B	0.057	0.054 - 0.076
7.5 - 9.5	A	0.115	0.090
7.5 - 9.5	B	0.080	0.069
10.5 - 12.0	A	—	0.068
10.5 - 12.0	B	—	0.040 - 0.035
10.5 - 12.0	A'	—	0.074

(\*) Slope from the semilogarithmic analysis.

The half wave potential of A' does not depend of pH, which indicates that this wave is due to the reduction of non-protonated aldimine.

The half-wave potential of B depends of pH in analogous form as the wave A does. However, according with Heyrovský and Vavricka (10), and as the protonation in solution is produced in a non-electroactive center --in wave B takes place the reduction of  $-\text{NO}_2$  group--, such dependence has not a simple physical meaning.

#### cyclic voltammetry.

In the cyclic voltammograms we can see the appearance of cathodic peaks, in accordance with the polarographic waves, as well as an other anodic peak, which is not observed if peak B has not appeared previously. Moreover, if we get peak A, the anodic peak decreases (Fig. 4). On the other hand, running a second cycle on the same drop causes the appearance of one or more new cathodic peaks (Fig. 5).

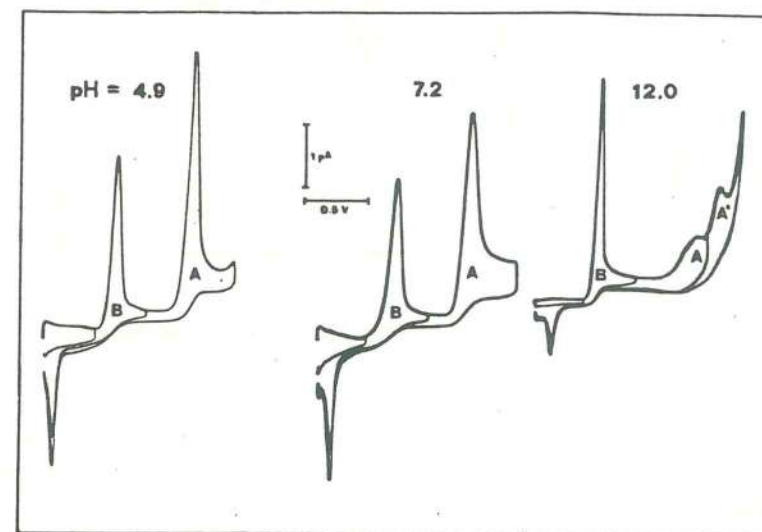


Figure 4.  
pH-dependence of voltammetric peaks of aldimine  $1.10^{-4}$  M.  
Started potential: +0.2, +0.1 and -0.2 V respectively.

This behaviour can be justified if we consider that peak B is due to the reduction of the  $-\text{NO}_2$  group; this reduction forms  $-\text{NHOH}$ , which is capable of being oxidized on the electrode --anodic peak--



giving  $-\text{NO}$ . The peak A, in neutral and acidic media, is due simultaneously to the reductions of the aldiminic bond and the  $-\text{NHOH}$  group to  $-\text{NH}_2$ . The peak that appears on a second scan, at more positive potential than peak B (Fig. 5), is due to the reduction of the  $-\text{NO}$  originated in the anodic process.

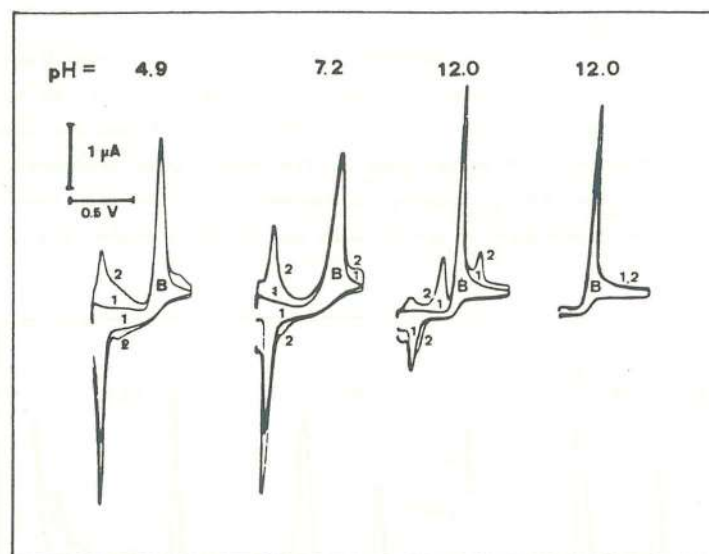


Figure 5.  
First and second scanning, on the same drop, at different pH values.

In the pH basic zone, when a second potential scanning is done, three new cathodic peaks appear (Fig. 5). As we have discussed previously, in process B (in these pH conditions) there is an ECE mechanism, and so the cathodic peaks can be due either to the nitroso derivative, its reaction products, or the ones of hydroxylaminealdimine. Fig. 5 demonstrates the necessity of the previous appearance of the anodic peak in order to get the cathodic ones and, therefore, we can conclude that the latter peaks are due to the nitroderivative and some of its products of reaction. Owing to their reactivity, these products can be derived from an intramolecular (tautomerization, etc) or an intermolecular reaction.

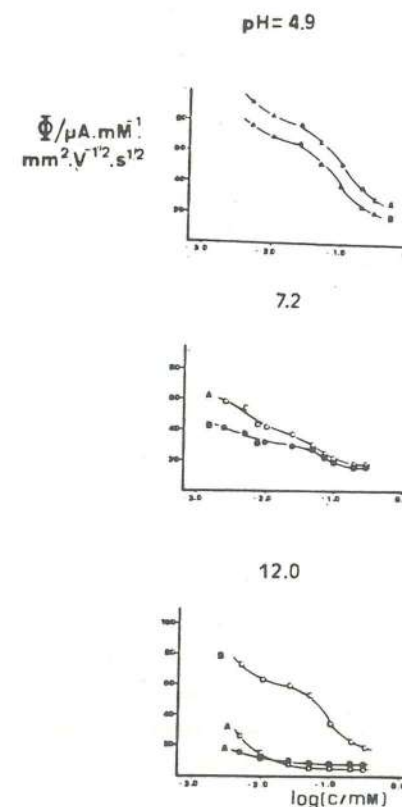


Figure 6.  
Concentration dependence of current function ( $i_p/c.A.v^{1/2}$ ) of peaks of aldimine at different pH values. Scan rate = 250 mV/s.

The current function,  $i_p/(c.A.v^{1/2})$ , of the different voltammetric peaks increases with the increase of the scan rate and with the decrease of concentration (Fig. 6), in a behaviour caused by the adsorption of the reactive species (11). For the peaks A and A' in basic medium, the current function is practically constant which indicates that, in these conditions, the electrode processes are fundamentally diffusion-controlled. The fact that adsorption of the aldimine is not appreciable now, is due to the competitive adsorption of other compounds of the solution (ethanol, etc) in the zone of appearance of these peaks.

#### controlled-potential electrolysis.

In acidic medium, the electrolysis at a potential corresponding to the limiting current of wave B, leads to the transfer of four electrons per molecule of aldimine, corresponding to the reduction of  $-\text{NO}_2$  group to  $-\text{NHOH}$ .

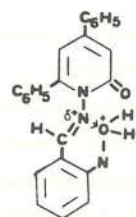
The electrolysis causes the disappearance of waves A and B and the appearance of a new wave at more negative potentials and another anodic one. This behaviour is due to the hydrolysis of the hydroxylamine formed in the reduction. This hydrolysis is favoured by the protonation in the hydroxylaminic oxygen that causes a polarization of the double bond  $>\text{C}=\text{N}-$ , as it is shown in

scheme I. This tautomeric form of the hydroxylamine has now a greater importance, because it is a substance present in the solution. The products of the hydrolysis are 1-amino-4,6-diphenyl-2-pyridone (identified in solution) and o-hydroxylaminobenzaldehyde. The mixture of these products causes the new cathodic wave, and the oxidation of the o-hydroxylaminobenzaldehyde the anodic one. Electrolyzing at potential corresponding to the wave A both waves disappear, and the number of transferred electrons is nearly ten (Table II), and 4,6-diphenyl-2-pyridone is identified in the solution. This indicates that wave A correspond to the reduction of aldiminic bond and of the  $\text{-NHOH}$  group to  $\text{-NH}_2$  also.

TABLE II

Coulometric determination of the number of electrons per molecule involved in the reduction of 1-(o-nitro-benzylideneamino)-4,6-diphenyl-2-pyridone in 60 % ethanolic Britton-Robinson buffer.

pH	wave	E (V)	n
4.0	B	-0.40	3.92
4.0	A + B	-1.00	9.75
5.5	B	-0.50	3.95
5.5	A + B	-1.20	9.80
7.2	B	-0.60	3.85
7.2	A	-1.30	5.90
9.3	B	-0.75	4.02
9.3	A	-1.45	5.95
12.0	B	-0.80	4.87
12.0	A + B	-1.45	6.10
12.0	A + A' + B	-1.70	9.90



SCHEME I

In neutral medium the reduction at the potential of the limiting current of the wave B also leads to the formation of hydroxylamine, with the difference that, now, this compound is stable. As a consequence, a transfer of four electrons per molecule is obtained, and the wave A is not altered with the electrolysis, while a new anodic wave, originated by the hydroxylamine, appears. In these conditions, if the electrolysis at potential corresponding to the limiting current of the wave A is done, the behaviour is identical to the described in acidic medium.

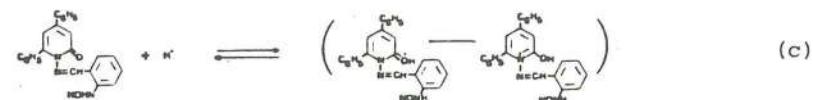
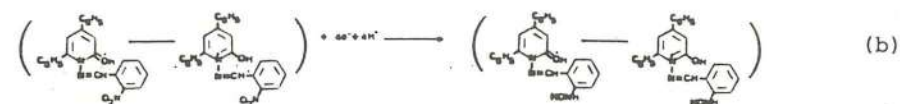
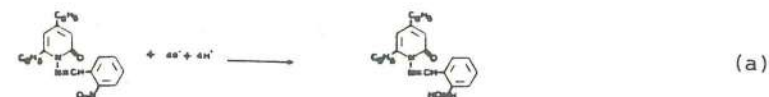
In basic medium, electrolyzing at the potential of the limiting current of the wave B, a number of electrons higher than four is obtained (Table II), which is due to the existence of the ECE mechanism previously described. Also, a pink colour is transitorily found during the electrolysis. This is the colour that one would observe if the hydroxylaminoaldimine formed in neutral medium is put in a basic solution. After the electrolysis waves are not obtained in the

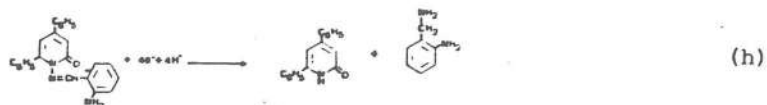
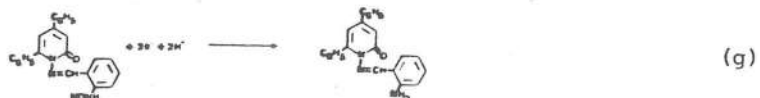
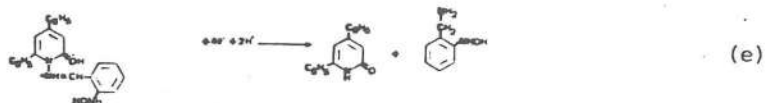
polarographic plots, and 1-amino-4,6-diphenyl-2-pyridone is detected in solution. The intermediate compound in this ECE mechanism is responsible for the pink colour. Its structure is difficult to predict, but it can be thought that is the result of the attack of the hydroxylaminic oxygen --which will be deprotonated enough in this pH conditions-- to the aldiminic carbon. 1-amino-4,6-diphenyl-2-pyridone will be the result of reduction and/or hydrolysis of this compound.

Electrolysis at a potential corresponding to the limiting current of wave A causes a transfer of six electrons per molecule (Table II) and in the latter polarographic plot, wave A' remains unaltered, and moreover anodic waves do not appear. So, in these conditions, the wave A is only due to the reduction of the hydroxylaminic group. In the wave A' the reduction of the aldiminic bond takes place with a transfer of four electrons, as it is shown by the presence of 4,6-diphenyl-2-pyridone in the solution, after the electrolysis.

#### REDUCTION MECHANISM.

According with preceding results and its correspondent discussion, the following mechanism can be proposed:





Wave B is originated by reaction (a) or (b), depending on pH. When aldimine is protonated (pH < 7) reaction (b) takes place, while if pH > 8 reaction (a) occurs. Wave A involves reactions (d) to (f), when pH < 7, and reactions (c) to (f) for pH > 8. In basic medium, wave A is caused by the reaction (g) and wave A' by the reaction (h).

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