RELATION OF AMINOMALONALDEHYDE TO REDUCTONES AND ITS POLAROGRAPHIC DETERMINATION

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Determination of aminomalonaldehyde (*III*) and its N-monosubstituted analogues *IV*, based on examination of their oxidation polarographic waves, was developed. This method was used to follow the alkaline hydrolysis of the salts *I* and *II* affording the aminodialdehydes mentioned. The relation of aminomalonaldehyde to the group of reductones is discussed.

We have recently devised an approach to the chemistry of aminomalonaldehyde (*III*) in which the key intermediate is represented by the quaternary salt *I* obtained by reaction of glycine with dimethylformamide and phosphorus oxychloride[1]. The diperchlorates *II*, derivatives of N-monosubstituted aminomalonaldehydes, can be approached quite similarly from N-monosubstituted glycines. Although the alkaline hydrolysis of the above mentioned salt *I* affords a solution containing the corresponding salt of the parent aminomalonaldehyde[1], the attempted liberation always resulted in polymerisation of the free aminomalonaldehyde. It was therefore desirable to develop an analytical method which would make possible to follow the course of the hydrolysis of the intermediate mentioned and to determine optimum conditions for the formation of aminomalonaldehyde. The structure of the aminoaldehyde *III* and its N-monosubstituted analogues *IV* is closely related to that of the simplest reductone, hydroxymalonaldehyde (*V*). Compounds derived from higher reductones by replacement of one or two enediol groups by the amino group have been paid attention some time ago[2,3]; it has also been observed that these analogues retained the reductive properties. It has been known on the other hand that reductone and the related enediol systems are polarographically active[4]. Polarographic waves could be therefore also expected with the present compounds.

$$[(CH_3)_2N-CH=C-CH=N(CH_3)_2]^{(+)} ClO_4^{(-)}$$
$$\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad X$$

I, X = —N=CH—N(CH₃)₂   *II*, X = [R—N=CH—N(CH₃)₂]^{(+)} ClO₄^{(-)}
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
a, R = CH₃
b, R = C₆H₅CH₂
c, R = C₆H₅

$$HO-CH=C-CH=O$$
$$|$$
$$X$$

III, X = NH$_2$

V, X = OH

VI, X = N(CH$_3$)$_2$

VII, X = CH$_3$CONH

IV, X = NHR

a, R = CH$_3$ *c*, R = C$_6$H$_5$

b, R = C$_6$H$_5$CH$_2$ *d*, R = (CH$_3$)$_2$CH

The object of the present paper is an analytical method developed on the basis of a preliminary examination on the polarographic behaviour of aminomalonaldehyde (*III*), of N-monosubstituted aminodialdehydes *IVa*—*IVc*, and particularly of N-isopropylaminomalonaldehyde (*IVd*), the only representative of this group which was obtained in a pure crystalline state[5].

EXPERIMENTAL AND RESULTS

Apparatus and Solutions

The current/voltage curves were taken on a LP7 polarograph with the use of an EZ7 linear recorder (Laboratorní přístroje, Prague) in connection with a capillary electrode with the drop time $t = 3$ s (80 cm of the Hg column) and the mercury outflow velocity $m = 1·86$ mg/s (with the open circuit). Saturated calomel electrode (S.C.E.) placed in the side arm of the Kalousek vessel was used as reference electrode. Orientation curves in a wide range of potentials were recorded at selected pH values (pH 1—13). Finer pH dependences of oxidation waves were examined with the use of the Britton and Robinson buffer solutions.

Materials

In the present polarographic investigations, N-isopropylaminomalonaldehyde[5] (*IVd*) served as the model compound. The aminoaldehyde *III* and its N-methyl, N-benzyl, and N-phenyl derivatives *IVa*—*IVc* were examined with the use of reaction solutions resulting after the alkaline hydrolysis of the starting salts *I* and *IIa*—*IIc*, the concentration of which was adjusted by dilution to $5 . 10^{-3}$M. As the reference compound, ascorbic acid was used; the oxidation half-wave potentials and their pH dependence are almost identical with this acid and the reductone[4].

Polarographic Behaviour of Aminomalonaldehydes *III* and *IV*

N-Isopropylaminomalonaldehyde (*IVa*) exhibits in the pH 1—7 region poorly developed reduction two-electron waves at negative potentials; their shape is deformed because of the final current rise due to decomposition of the electrolyte. At pH > 7 a decrease of the limiting current occurs and at pH 9 the waves on the capacity current curves are not perceptible any more. Quite analogous reduction waves were observed in the solution of the unsubstituted aminomalonaldehyde. In view of their character these reduction waves were not suitable for analytical purposes.

On the anodic branch of N-isopropylaminomalonaldehyde curves, a wave may be observed at pH > 4; the height of this wave corresponds to the uptake of two electrons (as compared with ascorbic acid and phthiocol under the same conditions). With the increasing pH value, the half-wave potential value of this wave undergoes a linear shift to more negative values (59 mV

per one pH unit). At pH > 9, another wave appears on the curve; this wave is approximately by 80 mV more positive and its $E_{1/2}$ *vs* pH dependence is also linear (80 mV per one pH unit). The limiting current of this more positive wave increases with the increasing pH value in the shape of a dissociation curve and in 0.1M-LiOH a value is achieved corresponding to the uptake of about 3 electrons. For purposes of comparison, the pH dependence of oxidation waves of ascorbic acid was examined. Thus, this acid affords at pH 6.8 a single two-electron wave and at pH 9.3 the curve exhibits an additional more positive wave which is exactly half as high while in 0.1M--LiOH ascorbic acid is oxidized in a single wave of the double height, *i.e.*, a four-electron wave.

In polarographic investigations of solutions after the alkaline hydrolysis of salts *I* and *IIa — IIc* anodic oxidation waves were obtained closely resembling those of N-isopropylaminomalonaldehyde by the shape, half-wave potential values, and behaviour in pH dependence. A single deviation manifested itself in the ratio of wave heights in the case of the phenyl derivative resulting by hydrolysis of the salt *IIc*; in contrast to the isopropyl derivative, the more negative wave of the phenyl derivative is twice as high at expenses of the wave at more positive potentials.

With the unsubstituted aminomalonaldehyde at pH > 12 the two waves coalesce; the hydrolysate of the salt *I* thus exhibits in dilute aqueous lithium hydroxide a single oxidation wave corresponding to the more negative step according to the $E_{1/2}$ value. Furthermore, the overall wave height is markedly greater than that of the single isopropyl derivative of the same molar concentration. In view of this observation, N-isopropylaminomalonaldehyde was not used as standard in analytical determinations. The half-wave potentials of all the derivatives examined were in 0.1M-LiOH identical within limits of experimental accuracy, namely, -0.23 V/s.č.e. for the more negative wave and -0.10 V/s.ce. for the more positive wave (maximum deviation, ± 5 mV). Attempted oxidation of dimethylaminomalonaldehyde[6] (*VI*) and acetamidomalonaldehyde[1] (*VII*) gave negative results.

Polarographic Determination of Aminomalonaldehydes

The analytical determination of aminomalonaldehydes was performed in dilute aqueous lithium hydroxide. Under these conditions the oxidation wave reaches the maximum height and exhibits a well developed plateau of the limiting current, the height of which is linear function of concentration. Moreover, the characteristic shape of the curve makes possible the qualitative identification of the aminodialdehyde.

TABLE I

Optimum Reaction Conditions in Hydrolysis of Perchlorates *I* and *II*

| Perchlorate	Concentration M	Aqueous NaOH M	Temperature °C	Time h
I	0·4	2	60	3
I	0·4	2	40	8
IIa	0·17	8	80	2
IIb	0·08	8	80	7
II	0·17	4	80	2

The hydrolysis of salts *I* and *II* was followed in such a manner that the appropriate salt (1 mmol) was introduced into 2·5—6·0 ml of preheated aqueous sodium hydroxide of the appropriate concentration (Table I), the reaction mixture was maintained at the temperature stated in a closed vessel, and samples (0·1 ml) were withdrawn in suitable time intervals. After the corresponding dilution, the content of the aminomalonaldehyde was determined by registration of the anodic curve under standard conditions and the time dependence of the height increases of the oxidation waves of products was recorded. In Table I conditions are shown under which maximum heights of anodic waves are obtained with the particular derivative. In the case of aminomalonaldehyde (*III*), the preparative experiments have shown that the hydrolysis of the salt *I* to the required product occurs by at least 90% under the conditions stated. The hydrolysis of salts *II* substituted on the nitrogen atom is considerably more difficult and the yield of the aminodialdehydes *IV* can be estimated only approximately (65—85%).

DISCUSSION

The present polarographic analysis of aminomalonaldehydes made possible to follow the hydrolysis of salts *I* and *II* and thus to find optimum conditions for the preparation of alkaline solutions of aminomalonaldehyde (*III*) and its N-monosubstituted derivatives *IV*.

Polarographic waves of aminomalonaldehydes are closely related to the reported[4] waves of the reductone or ascorbic acid. When compared with the corresponding wave of ascorbic acid, the oxidation waves of aminomalonaldehydes are shifted by about 30 mV to more positive values; this behaviour indicates a higher resistence towards oxidation in disagreement with the report of Micheel and coworkers[2] which state that the amino analogues of reductones are more sensitive to the aereal oxygen than the parent oxygen-containing reductone.

In the present work, we did not get any experimental evidence on the character of the product of the two-electron oxidation but it appears highly probable on the basis of analogy to the mechanism proposed for reductones that this product is of the type *VIII*, *i.e.*, a derivative of mesoxalic dialdehyde.

$$O=CH-C-CH=O$$
$$\underset{NR}{\overset{\|}{}}$$

VIII
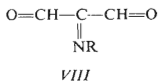
The formation of such a compound depends on the availability of at least one hydrogen atom on the nitrogen of the starting compound. In accordance with this idea, N,N-dimethylaminomalonaldehyde[6] (*VI*) does not afford in contrast to N-methylaminomalonaldehyde (*IVa*) the anodic wave under conditions of our experiments. N-Acetamidomalonaldehyde[1] (*VII*), the NH group of which is of the amide character, also does not undergo the polarographic oxidation. The oxidation at more positive potentials obviously results in more profound changes in the molecule. Concerning the analogy to reductones, the more positive wave of these compounds was mentioned

without comments by Brdička and Zuman[4] and a coalescence of two oxidation waves of ascorbic acid into one wave was observed[7] in sufficiently alkaline medium.

The present procedures for the determination of the content of aminomalonaldehyde and its N-monosubstituted derivatives in reaction solutions and the estimation of optimum conditions for the hydrolysis of salts *I* and *II* considerably facilitated the reactivity assays of these compounds and were repeatedly used in connection with some preparations[1,8,9].

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