Electroreduction and Related Studies on 2-Aminoacrylic Acid Derivatives. Part II.[1] Electroreactivity of 2-Acetamidoacrylic Acid

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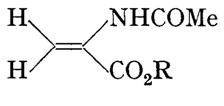
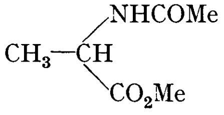
Polarographic, cyclic voltammetric, and potentiometric evidence indicates that at low pH values (<4) the mechanism of electroreduction of methyl α-acetamidoacrylate and α-acetamidoacrylic acid involves the protonation of a weak base in a thin layer near the electrode surface. As the protonated form of the substrate is removed by electrolysis, the electroactive substrate is replenished by a chemical reaction between the non-protonated species and a hydrogen ion. With increasing pH, a second wave appears on the polarograms. At high pH values (>4), methyl α-acetamidoacrylate is believed to be reduced in an ECE mechanism, *i.e.* a reversible charge transfer, followed by an irreversible protonation, followed by an irreversible charge transfer, where the number of electrons transferred in each step is one and $\Delta E = 0$.

N-ACETYLDEHYDROALANINE derivatives have been postulated to exist in tautomeric forms on the basis of their characteristic u.v. spectra.[2-4] Polarographic investigations of the reaction between pyruvic acid and amino-acids demonstrated the formation of an imino-compound postulated in transamination reactions.[5] Haffner and Wellner,[6] as well as Walsh *et al.*,[7] have presented evidence that imino-acids are produced in reactions catalysed by D- and L-amino-acid oxidases. Acid hydrolysis of dehydroalanine derivatives [8-11] results in the formation of pyruvic acid.

N.m.r. evidence has been obtained in this investigation indicating that there is no build-up of a stable imine tautomer of methyl α-acetamidoacrylate (2). This paper then considers the electroreduction of (2) and α-acetamidoacrylic acid (1). A comparison is made between the electroreduction of (1), (2), ethyl α-acetamidocinnamate,[1] and α-acetamidocinnamic acid.[1]



(1) R = H
(2) R = Me



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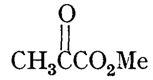

$$\mathrm{CH_3\overset{\overset{\displaystyle O}{\|}}{C}CO_2Me}$$

(4)

EXPERIMENTAL

General methods and instrumentation are given in Part I.[1]

α-Acetamidoacrylic Acid (1).—Compound (1) was prepared by boiling α,α-diacetamidopropionic acid [12-14] in a four-fold excess of glacial acetic acid.[12] The material had m.p. 200° (decomp.) (lit.,[12] 198—200°; [13] 204°), decolourized bromine water and was hydrolysed to pyruvic acid by HCl,[12] R_F 0·34 (silica gel; solvent D; [1] iodine vapour), δ [$(CD_3)_2SO$] 2·1 (3H, s, $NCOCH_3$), 5·1 (1H, d, *J* 1 Hz; *CH*:CNH, collapsed to a singlet upon shaking with D_2O), and 6·3 (1H, s, CH:C), δ (sodium salt in D_2O) 2·0 (3H, s, $NCOCH_3$), 5·6 (1H, s, CH:C), and 5·8 (1H, s, CH:C), δ (undissociated in D_2O) 2·1 (3H, s, $NCOCH_3$) and 6·1 (2H, s, CH_2:C).

Methyl α-Acetamidoacrylate (2).—Compound (2) was prepared by either boiling the silver salt of (1) [13] in an excess of methyl iodide or by the removal of HCl from methyl β-chloro-α-acetamidopropionate [13] with ethereal ammonia. The material had m.p. 51—53° (lit.,[14] 52—54°), R_F 0·75 (silica gel; solvent A; [1] u.v. light) and decolourized bromine water and the odour of pyruvic acid developed upon standing,[13] $\lambda_{max.}$ ($1M$-H_2SO_4) 237 nm ($\varepsilon \sim 3100$), $\lambda_{max.}$ [Britton–Robinson buffer (μ 0·5; pH 3·5)] 242 nm ($\varepsilon \sim 4000$), δ ($CDCl_3$) 2·1 (3H, s, N-$COCH_3$), 3·8 (3H, s, OCH_3), 5·9 (1H, d, *J* 1·4 Hz, *trans-CH*:CNH, collapsed to a singlet upon shaking with D_2O), 6·6 (1H, s, *cis-CH*:CNH), and 8·0 (1H, m, NH), δ (D_2O) 2·1 (3H, s, $NCOCH_3$), 3·8 (3H, s, OCH_3), and 6·0 (2H, s, CH_2:C).

±-Methyl N-*Acetylalanate* (3).—Compound (3) was prepared by the alcoholysis of the imidazolide [15] of ±-*N*-acetylalanine.[16] ±-*N*-Acetylalanine was suspended in $CHCl_3$ (30 ml) and *NN'*-carbonyldi-imidazole (Aldrich; 810 mg, 5 mmol) was added. After cessation of CO_2 evolution (40 min), methanol (15 ml) containing a catalytic amount of sodium methoxide was added to the homogeneous solution. Removal of the solvent (after 30 min) left an amber oil, R_F 0·6 (silica gel; solvent A; [1] iodine vapour), δ ($CDCl_3$)

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[1] Part I, D. N. Schluter, G. Mamantov, and J. R. Vercellotti, preceding paper.

[2] D. Shemin and R. M. Herbst, *J. Amer. Chem. Soc.*, 1938, **60**, 1954.

[3] C. E. Carter and J. P. Greenstein, *J. Nat. Cancer Inst.*, 1946, **7**, 51.

[4] V. E. Price and J. P. Greenstein, *J. Biol. Chem.*, 1947, **171**, 477.

[5] M. Brezina and P. Zuman, 'Polarography in Medicine, Biochemistry, and Pharmacy,' Interscience, New York, 1958, p. 564.

[6] E. Hafner and D. Wellner, *Proc. Nat. Acad. Sci. U.S.A.*, 1971, **68**, 987.

[7] C. Walsh, A. Schonbrunn, and R. A. Abeles, *J. Biol. Chem.*, 1971, **246**, 6855.

[8] I. Photaki, *J. Amer. Chem. Soc.*, 1963, **85**, 1123.

[9] I. Photaki and V. Bardakos, *J. Amer. Chem. Soc.*, 1965, **87**, 3489.

[10] A. E. Leutzow and J. R. Vercellotti, *J. Chem. Soc.* (*C*), 1967, 1750.

[11] G. Riley, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 1957, 1373.

[12] M. Bergmann and K. Graffe, *Z. physiol. Chem.*, 1930, **187**, 187.

[13] E. Rothstein, *J. Chem. Soc.*, 1949, 1968.

[14] J. P. Greenstein and G. Carter, *J. Nat. Cancer Inst.*, 1946, **7**, 57.

[15] H. A. Staab and W. Rohr, 'Newer Methods of Preparative Organic Chemistry,' ed. W. Foerst, Academic Press, New York, 1968, vol. 5, pp. 61—108.

[16] L. A. Fieser, 'Organic Experiments,' Heath, Boston, 1964, p. 138.

1·41 (3H, d, *J* 7 Hz, CH_3CH), 2·03 (3H, s, $NCOCH_3$), 3·80 (3H, s, OCH_3), 4·4—4·8 (1H, m, CH, partially collapsed upon shaking with D_2O), and 5·6—5·8 (1H, m, NH, collapsed upon shaking with D_2O).

Methyl Pyruvate (4).—Compound (4) was prepared by a modification of Weissberger and Kibler's procedure.[17] Freshly prepared pyruvic acid [18] (22 g), dry methanol [19] (32 g), benzene (88 ml), and toluene-*p*-sulphonic acid (0·1 g) were refluxed in a round bottom flask (150 ml) fitted with a Soxhlet extractor containing anhydrous $MgSO_4$ for 12 h. The fraction boiling at 135—138° (lit.,[17] 136—140°) was collected, δ [Me_4Si–CF_3CO_2H–$CDCl_3$ 1 : 79 : 20 (w/w)] 2·50 (3H, s, CH_3CO) and 3·83 (3H, s, OCH_3).

RESULTS

N.m.r. Investigations to determine the Presence of Stable Immonium Ions.—N.m.r. results indicate that (2) in $CDCl_3$ and trifluoroacetic acid (TFA) hydrolyses to acetamide and methyl pyruvate. Compound (2) was dissolved in $CDCl_3$ (1 ml) and then diluted with TFA (1 ml). After 10 days, the spectrum exhibited three singlets at δ 2·33 (CH_3 group of acetamide), 2·60 (CH_3 group of methyl pyruvate), and 4·01 (OCH_3 group of methyl pyruvate). The solution was then evaporated to dryness. The remaining solid was dissolved in D_2O, and the n.m.r. spectrum exhibited a singlet at δ 2·00. When Na_2CO_3 was added to the D_2O solution a singlet at δ 2·00 was observed. The n.m.r. spectra of an authentic sample of acetamide in both D_2O and in 0·1M-DCl exhibit singlets at δ 2·00.

A sample was prepared containing acetamide (48·6 mg) and methyl pyruvate (110 mg) dissolved in 500 µl of a solution of 1 : 79 : 20 by weight of Me_4Si, $CDCl_3$, and TFA, respectively. N.m.r. spectra recorded at various times (to 150 h) exhibited three singlets which remained constant. The singlets at δ 2·10, 2·50, and 3·83 are attributed to acetamide and the methyl and the methoxy-group of pyruvate ester, respectively.

When (2) (133 mg) was dissolved in the 1 : 79 : 20 mixture of Me_4Si, $CDCl_3$, and TFA, the formation of methyl pyruvate and acetamide was confirmed by the comparison of its spectrum to that of the authentic mixture of acetamide and methyl pyruvate. After 230 h approximately 4% of (2) was hydrolysed to acetamide and methyl pyruvate.

When (2) was dissolved in D_2O and then treated with Na_2CO_3, n.m.r. data indicated that the only reaction that occurred was the saponification of the ester. This is indicated by the formation of three new singlets at δ 3·30 (methanol), 5·61 (H *trans* to the acetamido-group of the anion of α-acetamidoacrylic acid), and 5·83 (H *cis* to the acetamido-group of the anion of α-acetamidoacrylic acid). Upon dilution of the sample with 38% DCl in D_2O, the singlets at δ 5·16 and 5·83 collapsed to a singlet at δ 6·30. When methanol was added, the singlet at δ 3·30 increased. An n.m.r. spectrum of the sodium salt of α-acetamidoacrylic acid in D_2O gave singlets at δ 2·10, 5·78, and 5·89. Upon neutralizing the sample with DCl the two signals at δ 5·78 and 5·89 collapsed to a singlet at δ 6·1.

When a 0·066M solution of (2) in 0·139M-DCl in D_2O was prepared, the solution became very viscous and the n.m.r. spectrum produced two signals, wide envelopes at δ 1·8—2·1 and 3·6—3·8. The doublet (olefinic protons) at δ 6·0 disappeared. This behaviour indicates that polymerization occurred since the olefinic proton signals disappeared. Polymerization of (2) was encountered several times during this investigation, both during purification and in the preparation of stock solutions for polarographic analysis. The polymerization of (2) has been studied.[20]

Polarographic Studies of Methyl α-Acetamidoacrylate (2) *in Acidic Media.*—Compound (2) exhibits two reduction waves (Figure 1). Wave I, which is observed at low pH values, could only be evaluated by means of derivative polarography since the $E_{\frac{1}{2}}$ values were very near the decomposition potentials of the buffer solutions. Wave I decreased with increasing pH and was replaced by a second more cathodic wave (wave II).

Plots of i_k/i_d (as previously defined) [1] and of $-E_{\frac{1}{2}}$ *vs.* pH are shown in Figure 1. The other experimental parameters obtained for (2) at low pH values were the variation of the limiting current with concentration (Figure 2) and log $i^{\frac{2}{3}}/(i_d - i)$ *vs.* *E* plots (Figure 3). An examination of Figure 2 shows that the limiting current for wave I at pH 2·5 is not linear with concentration as is the case for wave II at pH 9·5. It was not possible to obtain accurate limiting currents at concentrations smaller than 1mM because of the high background current. The plot of log $i^{\frac{2}{3}}/(i_d - i)$ as a function of *E* (Figure 3) is linear at small currents but bends upward near the plateau of the wave. This anomaly will be discussed later.

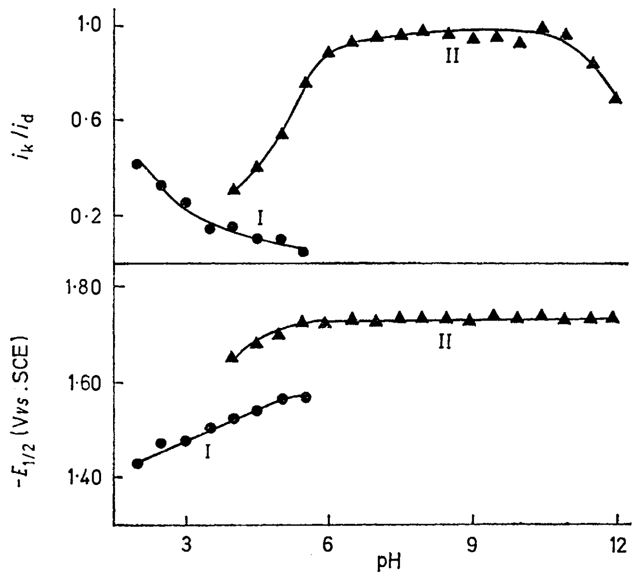

FIGURE 1 Dependence of limiting currents and half-wave potential on pH for (2)

Polarographic Studies of Methyl α-Acetamidoacrylate (2) *in Alkaline Media.*—Better experimental results were obtained for the reduction of (2) at higher pH values. Wave II appeared to be irreversible using the criterion of change in slope of the log *i*–log *t* plot for the instantaneous current obtained on the rising portion of the polarographic wave,[21] *i.e.* from 0·43 near the foot of the wave to 0·19 at the plateau.

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[17] A. Weissberger and C. J. Kibler, *Org. Synth.*, 1955, **3**, 610.

[18] J. W. Howard and W. A. Fraser, *Org. Synth.*, 1943, **1**, 475.

[19] C. K. Mann in 'Electroanalytical Chemistry,' ed. A. J. Bard, Marcel Dekker, New York, 1969, vol. 3, pp. 57—134.

[20] S. S. Ivanov, L. B. Nadezhdina, and I. M. Stasenkova, *Polymer Sci. U.S.S.R.*, 1963, **5**, 1411.

[21] J. Kuta and I. Smoler, 'Progress in Polarography,' eds. P. Zuman and I. M. Kolthoff, Interscience, New York, 1962, vol. 1, pp. 43—63.

The slopes of the log i–log t plots on the plateaux of the waves were found to be approximately 0·2 for pH 8—10 as required by theory [21,22] for diffusion-controlled waves.

The limiting current was linear with increasing concentration and the plot passed through the zero point (Figure 2).

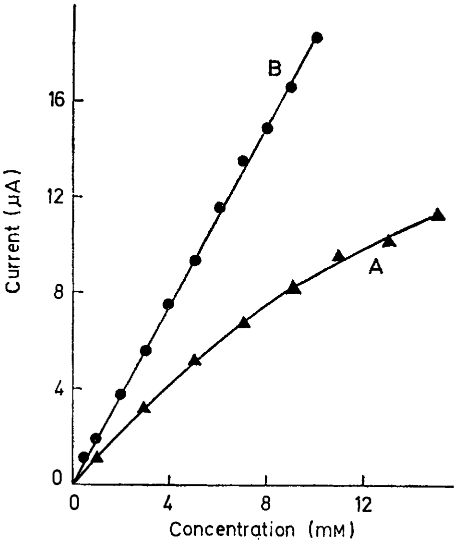

Figure 2 Dependence of limiting current on concentration for (2) at: A, pH 2·5; B, pH 9·5

The half-wave potentials were independent of pH at values >5 and of concentration. Controlled potential electrolysis (CPE) experiments performed in a 0·5M-phosphate buffer at pH 7·6 gave an n value of 2. This value of 2 was verified by the fact that the only product which was isolated was ±-methyl N-acetylalanate (3). Identification of the electrolysis product was made by comparing its n.m.r. spectrum with that of an authentic sample of (3) prepared by an independent method.

In the construction of the pH profile, it was necessary to extrapolate the current to zero time at pH >10·5 in order to obtain the limiting current. The half-lives (s) for the disappearance of (2) were 63, 67, 190, and 690 in 0·2N-NaOH, pH 12·0, 11·5, and 11·0, respectively.

The plots of E vs. log $i/(i_d - i)$ were linear and had slopes of ca. 60 mV. The slope of 60 mV is consistent with either an irreversible two-electron transfer with the transfer coefficient (α) having a value of 0·5, or a reversible one-electron transfer followed by an irreversible chemical reaction (protonation) slower than the electron transfer (the total number of electrons per mole is 2, as shown by CPE).[23] In the second case subsequent addition of another electron and proton does not affect the half-wave potential.[23] The half-wave potential is independent of pH, as would be expected if water is the most important proton donor.[23] The answer to the problem of whether the mechanism of reduction for compound (4) in alkaline media was simply a two-electron irreversible process or an ECE [24] process could only be found by cyclic voltammetry experiments.

Cyclic Voltammetry Experiments in Alkaline Solutions.— Plots of the variation of $i_p/v^{\frac{1}{2}}$ as a function of v were consistent [25] with the mechanism which involves a reversible electron transfer, followed by an irreversible chemical reaction, which in turn is followed by an irreversible charge transfer, where the number of electrons are equal and the half-wave potentials are identical. The cyclic voltammograms which were obtained did not exhibit an anodic wave at slow scan rates, but as Nicholson and Shain [25] point out, the anodic wave is sometimes hard to detect. Because of the irreversibility of the chemical step and the second charge transfer step, the anodic wave could not be detected at slow scan rates. At scan rates >50 V s^{-1}, an anodic wave was detected on the voltammograms.

Electrochemical Reduction of α-Acetamidoacrylic Acid (1).— Few experimental parameters could be obtained for (1) because the half-wave potentials were so cathodic. Derivative polarography was essential to characterize the electrochemical behaviour of (2); thus, any rationalization of the electrochemical behaviour of (1) must be made by comparing the experimental parameters which were obtained for it with those for (2) as well as for ethyl α-acetamidocinnamate [1] and α-acetamidocinnamic acid.[1]

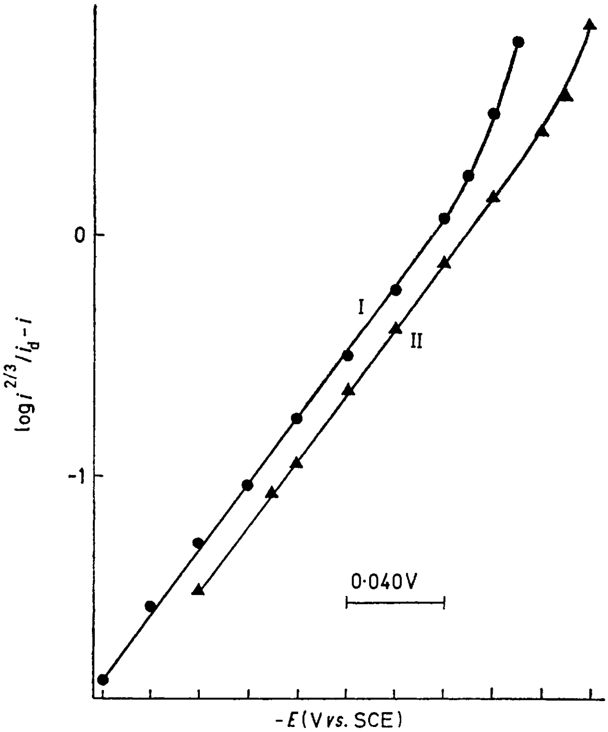

Figure 3 Plot of log $i^{\frac{2}{3}}/(i_d - i)$ for (2) at pH 2·5: I 15mM; II 5mM. Potentials start at −1·380 and −1·400 V for I and II, respectively. The plots have been shifted on the potential axis for clarity

Two waves were observed for (1). Wave I decreased with increasing pH and was replaced by a more cathodic wave which also decreased until it disappeared near pH 8. Plots of the limiting currents and half-wave potentials as a function of pH are shown in Figure 4.

DISCUSSION

Any proposal of a reaction mechanism for the reduction of (2) at low pH values has to be speculative because of the lack of data. A probable mechanism which is

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[22] I. Smoler, *J. Electroanalyt. Chem.*, 1963, **6**, 465.

[23] C. L. Perrin, *Progr. Phys. Org. Chem.*, 1965, **3**, 194.

[24] D. N. Schluter, Ph.D. Dissertation, University of Tennessee, 1972.

[25] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1965, **37**, 178.

based on our results is shown in Scheme 1 where k_d and k_r have been previously defined.[1]

Experimental evidence [1] established the fact that the more anodic waves observed in the reduction of ethyl α-acetamidocinnamate and α-acetamidocinnamic acid were due to protonation of the substrate at the DME. Similar behaviour for (2) would be expected because of structural similarities and because the pK_a for (2) is only *ca.* 0·5 pK_a unit more negative than for ethyl α-acetamidocinnamate. The pK_a values of (1) and (2) determined by potentiometric titration in glacial acetic acid were −1·50.[24]

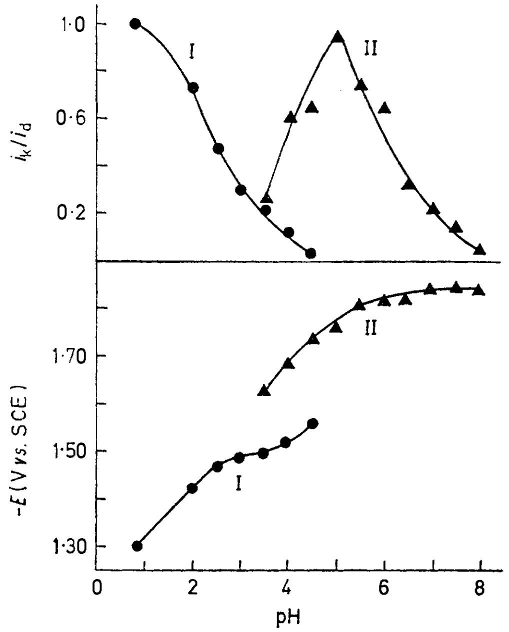


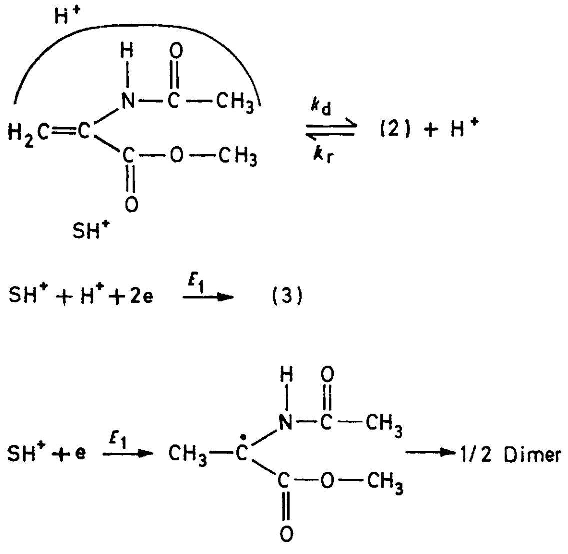
FIGURE 4 Dependence of limiting currents and half-wave potentials on pH for (1)

A similar mechanism involving protonation has been found for the electroreduction of fumaric and maleic acids [26] and for acetophenone.[27]

Because the height of the first wave is much smaller than the maximum limiting current and because the sum of the currents for waves I and II over the entire pH range is not constant, dimer formation can be expected to be a factor as in the reduction of acetophenone,[27] where a one-electron wave is observed at low pH values; the height of the wave decreases in the form of a dissociation curve as the pH is increased. At high pH values, this is replaced by a more cathodic wave which has a height corresponding to a two-electron wave. At extremely high pH values, this diminishes to the level of a one-electron wave and an additional wave appears at a more cathodic potential. Mairanovskii and Pavlov [27] have interpreted this behaviour as a protonation of the substrate at the DME followed by dimerization at low pH values. At medium pH values, *i.e.* 7—10, the resulting radical anions are protonated and further reduced (ECE). At high pH values, the radical anions cannot undergo protonation and thus are further reduced at a more cathodic potential (EE mechanism, *i.e.* electrical-chemical-electrical-chemical). Dimerization at low pH values has been observed for aliphatic polyenic aldehydes [28] and phenyl vinyl ketone [29] as well.

Deviations from linearity of the limiting current with increasing substrate concentration may indicate a higher order of reaction.[30] Compound (2) exhibits this behaviour.

Another experimental parameter which was obtained to substantiate the fact that dimer formation might be a factor in the electrochemical reduction of (2) at low pH values was the plot of log $i^{\frac{2}{3}}/(i_d - i)$ as a function of E (Figure 3). For a reduction mechanism which involves dimer formation, this plot is linear at low substrate concentrations and short drop times.[31] At sufficiently high concentrations, *i.e.*, > 1mM, such a curve bends downward. Mairanovskii [31] claims that this is due to the gradually increasing retardation of the electrode process caused by the adsorbed products of reduction as the current increases along the wave. The higher the concentration, the more the upper part bends. In the lower part of the wave, the experimental points obtained at various concentrations lie on the same line.[31] Since it was not possible to obtain usable polarograms at concentrations <5mM, adsorption effects could not be determined; nor could adsorption be studied by cyclic voltammetry because of the very cathodic potentials. In Figure 3, the plots of log $i^{\frac{2}{3}}/(i_d - i)$ *vs.* E bend upward. This could possibly be caused by the contribution of



SCHEME 1

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[26] L. Pospisil and J. Kuta, *Coll. Czech. Chem. Comm.*, 1969, **34**, 1804.

[27] S. G. Mairanovskii and V. N. Paulov, *Zhur. fiz. Khim.*, 1964, **38**, 1804.

[28] S. G. Mairanovskii, L. A. Yanovskaya, N. V. Kondratova, and G. V. Krishtal, *Elektrokhim.*, 1968, **4**, 1127.

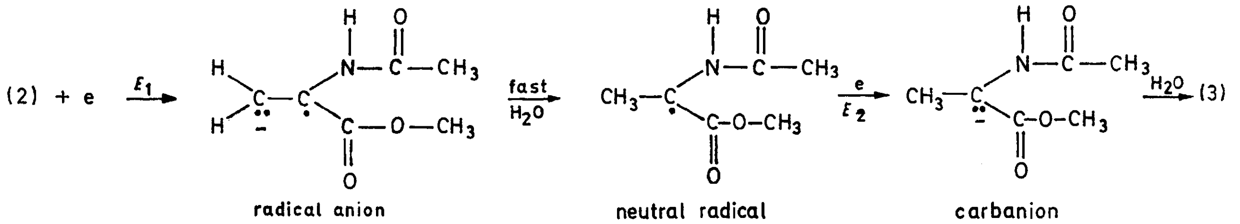
[29] P. Zuman and J. Michl, *Nature*, 1961, **192**, 655.

[30] P. Zuman, *Progr. Phys. Org. Chem.*, 1967, **5**, 126.

[31] S. G. Mairanovskii, 'Progress in Electrochemistry of Organic Compounds,' eds. A. N. Frumkin and A. B. Ershler, Plenum Press, London, 1971, p. 96.

wave II. The reciprocal slope of the linear portion of these plots was 73 mV^{-1} which would reflect irreversibility.[27]

Since it was not possible to investigate the electrochemical behaviour of (2) at low pH values by controlled potential electrolysis because background processes were too large, the verification of mechanism for dimer formation was not made. Dimer formation can only be postulated on the basis of comparisons with known systems, log $i^{\frac{2}{3}}/(i_d - i)$, limiting current–concentration, and i_k/i_d plots. Additional work is in progress.



SCHEME 2

In view of the fact that no stable imine tautomer was observed for (2) by n.m.r. spectroscopy and that no wave for pyruvic acid was observed on the polarograms, a mechanism which involves a tautomeric species is ruled out.

In contrast to the electrochemical behaviour of (2) at low pH values, the experimental parameters obtained at alkaline pH values, *i.e.* log $i/(i_d - i)$ *vs.* E, log i—log t, and $i_p/v^{\frac{1}{2}}$ plots, and controlled potential electrolysis point to Scheme 2 as the mechanism for the reduction of (2) in alkaline solutions ($E_1 = E_2$). This mechanism operates for other olefins, *i.e.* $E_{\frac{1}{2}}$ is independent of pH and a log plot is that for a reversible one-electron transfer.[32,33]

The gradual decrease in the polarographic limiting current for (2) at pH values >10 cannot be explained at present. Saponification can be ruled out since the limiting currents were extrapolated to zero time.

The decreasing current for the first wave of (1) as the pH is increased is consistent with the preprotonation steps proposed for (2), ethyl α-acetamidocinnamate,[1] and α-acetamidocinnamic acid.[1] Three waves were observed on the polarograms for α-acetamidocinnamic acid.[1] A third wave corresponding to the reduction of the carboxylic anion of (1) was not seen, probably due to the discharge of the supporting electrolyte. In contrast to (2), the current for (1) is greater at low pH; but the total current, unlike that of the phenyl analogues, is not constant. Dimer formation could possibly contribute to the decrease in the total current near pH 3·0 as it has been shown that the reduction of (2) might involve dimer formation.

Summary of the Electrochemical Reduction of Dehydroalanine Derivatives.—An examination of the curves in Figure 5, which are the i_k/i_d plots for the dehydroalanine derivatives studied, reveals that an overall mechanism can be ascribed to the electrochemical reduction. At low pH, all the compounds are protonated in the vicinity of the mercury electrode and reduced in that form. As the protonated form is removed by electrolysis, it is replenished by the chemical reaction between the non-protonated species and hydrogen ions. As the pH is increased, the rate of this chemical reaction decreases and two waves are observed on the polarograms. The first wave represents the reduction of the protonated form and the second wave, the non-protonated form. For the acids, a second acid–base equilibrium system[34] is conceivable and can be ascribed to the dissociation of the carboxy-protons.

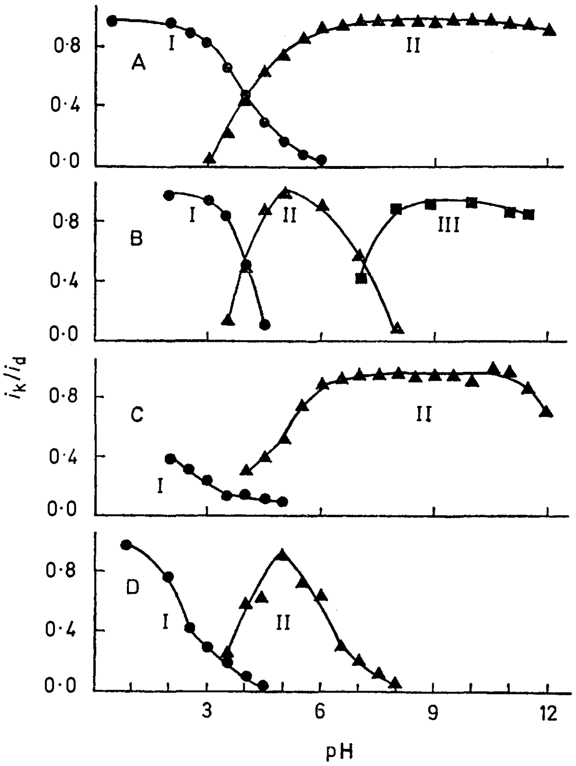


FIGURE 5 Dependence of limiting currents of: A ethyl α-acetamidocinnamate (ref. 1); B α-acetamidocinnamic acid (ref. 1); C compound (2): D compound (1)

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[32] S. Wawzonek and J. W. Fan, *J. Amer. Chem. Soc.*, 1946, **68**, 2541.

[33] J. Volke and J. Holubek, *Coll. Czech. Chem. Comm.*, 1962, **27**, 1777.

[34] J. Heyrovsky and J. Kuta, 'Principles of Polarography,' Academic Press, New York, 1965, p. 368.

The anomalies which are observed in Figure 5 can be rationalized as follows: the observed low $i_{\mathrm{k}}/i_{\mathrm{d}}$ values seen for (2) at low pH may be attributed to the dimerization of the reduction product. The log $i^{\frac{2}{3}}/(i_{\mathrm{d}} - i)$ *vs.* E plot and the nonlinear dependence of the limiting current on concentration (Figures 2 and 3) point to dimerization. The absence of a third wave for (1) can be ascribed to a very cathodic half-wave potential. The decrease in the $i_{\mathrm{k}}/i_{\mathrm{d}}$ values for the most cathodic waves of (2) and the α-acetamidocinnamic acid derivatives could possibly be due to a change in mechanism of reduction. Finally, the reduction of (2) at the higher pH values is assigned an ECE [25] mechanism.

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