

Electrochemical Reduction of Acetylacetone in Hydrochloric Acid

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The electrochemical reduction of acetylacetone on a mercury cathode in aqueous hydrochloric acid medium has been studied. It has been shown that the electroactive species is the protonated form of acetylacetone. The experimental results indicate that the rate of electrochemical reduction is dependent upon the preceding chemical protonation step and/or adsorption of the electroactive species. The electrolysis at controlled potential (-1.2 V *vs.* S. C. E.) yielded the following products: acetaldehyde, acetone, acetic acid, 2,5-hexanediol and 2,5-dimethyltetrahydrofuran. Possible mechanistic routes leading to the formation of these products are discussed.

The electrochemical reduction of ketones has been extensively studied¹. Depending on the reaction conditions used in electrochemical reduction, various compounds (pinacols, alcohols, metalloorganic compounds and alkanes) can be formed. By the presence of other carbonyl groups in a molecule the number of possible products is increased.

Various diketones were a particularly interesting subject for electrochemical study, not only because of the numerous possibilities for reduction pathways, but also because of potential synthetic use. Reduction of 1,2-diketones gave α -hydroxy ketones². D. H. Evans *et al.*³⁻⁶ and E. Kariv *et al.*⁷⁻¹⁴ extensively studied the electrochemical behaviour of 1,3-diketones, which were shown to be affected by intramolecular interaction between two carbonyl groups. A. D. Thomsen and H. Lund¹² reported very interesting work on the electrochemical reduction of acetylacetone in hydrochloric acid media. B. N. Gourley and J. Grimshaw¹³ have studied the reduction of some 1,5- and 1,6-diketones by polarography and product studies.

E. Kariv and B. J. Cohen¹⁴ have extended their interest to the research on intramolecular interaction between carbonyl groups in 1,4-diketones, which was the first report in electrochemical literature on this subject. They investigated the reduction of cyclohexane-1,4-dione and acetylacetone in water and water-propane-2-ol mixture as solvent and tetraethylammonium *p*-toluenesulphonate as supporting electrolyte. Reduction of cyclohexane-1,4-dione yielded five products, while the preparative reduction of acetylacetone at -2.3 V *vs.* S.C.E. yielded no product and acetylacetone was quantitatively recovered.

This work prompted us to find suitable conditions for the reduction of acetylacetone in order to study its electrochemical behaviour. We have

found that acetonylacetone was reducible in the aqueous hydrochloric acid medium in which its reduction was studied in this work.

RESULTS AND DISCUSSION

A reduction wave for acetonylacetone was obtained in aqueous hydrochloric acid solution* (Fig. 1.). The limiting current of the polarographic wave presented in Fig. 1. is slightly decreasing when HCl concentration changed from 0.5 to 0.01 M; half-wave potential is shifted more cathodically (from -1.13 V at 0.5 M to -1.27 V at 0.01 M HCl).

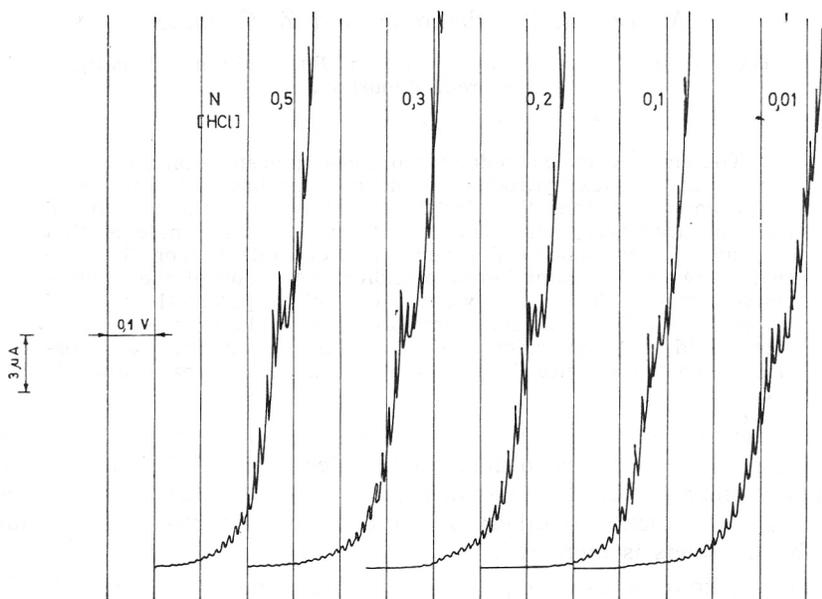


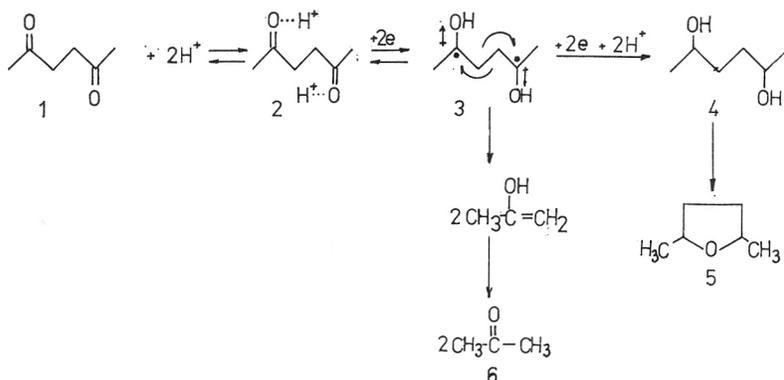
Fig. 1. Polarographic behaviour of acetonylacetone (3.2×10^{-2} M) at different HCl concentrations starting at -0.9 V vs. S. C. E.

Polarographic behaviour of acetonylacetone 1 in a solution of changing HCl concentration shows that the rate of electrochemical reduction of acetonylacetone is dependent on the concentration of hydrogen ions¹⁷.

The limiting currents of the reported polarographic waves are much smaller than those expected for a diffusion controlled process. These experimental results indicate that the electroactive species is not acetonylacetone 1, which probably exists in the solution in several forms and only one of them is electroactive (scheme 1).

* Between pH 3 and 14 in buffered solution (Britton-Robinson buffers) no polarographic wave was observed. In some earlier papers S. I. Vityaeva and A. L. Markman^{15,16} reported two waves on the polarogram of acetonylacetone obtained with lithium chloride and tetraethylammonium iodide as supporting electrolyte in aqueous media.

* The linear plot $i_L - h$ passes practically through the origin.



The results presented in Fig. 2 show the influence of the concentration of hydrochloric acid and of the height of the mercury reservoir on the limiting current*. Further increase of concentration of acetonylacetone (above 6×10^{-2} M) does not alter the rate of reaction significantly, indicating that the rate of electrochemical reduction is controlled by the reaction of protonation of acetonylacetone and/or by the adsorption of electroactive species 2.

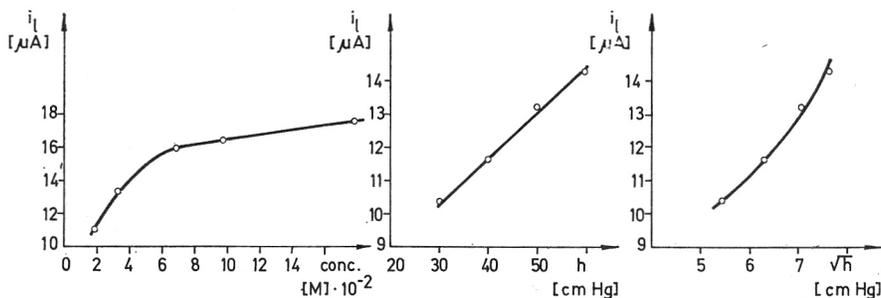


Fig. 2. Influence of concentration of acetonylacetone and height of the mercury reservoir (concentration of acetonylacetone: 3.2×10^{-2} M) on the limiting current. Supporting electrolyte: 0.5 M HCl.

Polarization curves obtained with a large mercury cathode (cca 19 cm^2) show that the initial reduction potential, which could be determined by extrapolating the current-potential curve to zero current (Fig. 3), becomes more negative as the concentration of acetonylacetone in the solution increases. This effect could be explained by saturation of the electrode surface by the adsorbed reactant and/or reaction products formed during reduction. A similar effect was noted by several workers^{18,19}.

Logarithmic analysis of the polarographic curves, taken from Fig. 1 indicates that the electrochemical reduction of acetonylacetone in 0.5 M HCl is a reversible process. Plotting of E (the applied potential) vs. $\log [(i_L - i)/i]$ gave straight line with a slope of 25 mV.

The reduction of acetonylacetone in 0.5 M aqueous HCl solution was also studied by means of preparative electrolysis and products distribution. Major

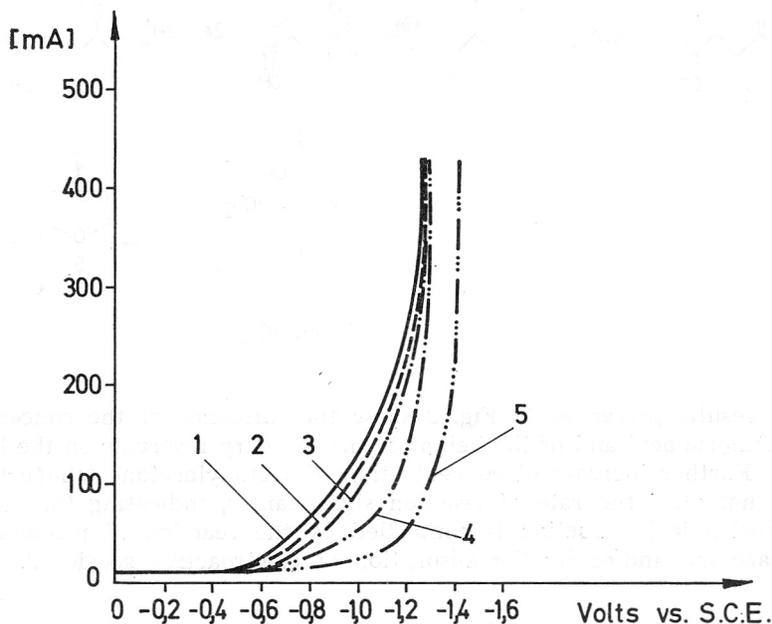


Fig. 3. Polarization curves at large mercury cathode for different concentrations of acetonylacetone.

1. 0.032 M, 2. 0.065 M, 3. 0.130 M, 4. 0.325 M, 5. Supporting electrolyte: 0.5 M HCl

products were isolated by preparative gas chromatography and examined by i.r., n.m.r., and mass spectrometry. In the case of minor products (acetaldehyde and acetone) their identification was performed by comparison of g. c. retention times with those of authentic samples. Between several other unidentified compounds we have found organo-mercury compounds whose structure is under investigation at present. The yields of products, after electrolysis at -1.2 V vs. S. C. E., are shown in the Table.

TABLE

Composition of the Reaction Mixture obtained by Electrolysis of 0.13 M Acetonylacetone in Aqueous 0.5 N HCl Solution at -1.2 V vs. S. C. E.^{a,b}

Products	Yield (%)
Acetaldehyde	2
Acetone	4
Acetic acid	5
2,5-dimethyltetrahydrofuran	10
Acetonylacetone (unreacted)	35
2,5-hexanediol	26
Not defined	18

^a Amount of electricity passed: 2000 C

^b Amount of acetonylacetone reduced: 2 ml

The first step in the reduction is addition of two electrons to protonated acetylacetone 2, which is the electroactive species forming the diradical 3 (scheme 1). The conversion of the diradical 3 into the main product 2,5-hexanediol 4 may occur by further addition of two electrons through formation of a dianion following its protonation. A mixture of diastereoisomeric 2,5-hexanediols was obtained in the electrochemical reduction of acetylacetone. It is known²⁰ that the eliminative cyclisation of disecundary 1,4-diols, leading to the formation of tetrahydrofurans 5, proceeds stereoselectively by S_N2-type mechanisms with inversion of configuration at one chiral centre. The cyclisation of meso 2,5-hexanediol leads to the formation of *trans*-2,5-dimethyltetrahydrofuran, while the respective diastereoisomeric substrates are converted exclusively into *cis*-2,5-dimethyltetrahydrofuran. By g. l. c-analyses we have found that the ratio *meso/dl* 2,5-hexanediols, after electrolysis at -1.2 V vs. S. C. E., was about one.

We feel that formation of acetaldehyde and acetic acid, which are rather unusual products of electrochemical reduction, might be explained by homolytic degradation of starting compounds by means of present radicals, but this hypothesis needs to be tested.

The formation of acetone 6 through cleavage of diradical 3 is due to 1,4-interaction, since the direct cleavage of such a bond is not known to occur in the potential range studied here. A similar cleavage was postulated in electrochemical reduction¹⁴, Clemmenson reduction²¹ and reduction with lithium in liquid ammonia²².

The stereochemistry of the electrode reaction during the reduction of acetylacetone, as well as some other 1,4-diketones is under investigation in our laboratory.

EXPERIMENTAL

Gas chromatography

A Varian Aerograph instrument series 1200 (flame ionisation detector) or a Perkin-Elmer F-11 instrument was used for analytical work, and a Varian Aerograph instrument model A-700 (thermistor detector) for preparative purposes, with columns Carbowax 20M, Poropak Q or 1,2,3-tris-(2-cyanoetoxy)-propane adsorbed on Chromosorb P. Other conditions for gas chromatography analyses were similar to those described in our previous work²³. Separations of *cis*-2,5-dimethyltetrahydrofuran (shorter retention time) and *trans*-2,5-dimethyltetrahydrofuran (longer retention time) were performed using a 1,2,3-tris-(2-cianoetoxy)-propane column.

Spectroscopic methods

N. m. r. spectra were recorded on a Varian A-60A spectrometer (CCl₄ was used as solvent and tetramethylsilane as internal standard), i. r. spectra on a Perkin-Elmer Infracord instrument model 337 and mass spectra on a Varian mass spectrometer CH5.

Polarography

Polarograms were recorded on a Polariter PO4-polarograph (Radiometer Copenhagen). The cell used was a modified H-type of 25 ml capacity with dropping mercury electrode and saturated calomel electrode connected *via* a salt bridge of 3% agar in saturated potassium chloride solution. Temperature was kept constant at 25.0 ± 0.1 °C by means of a thermostat.

Preparative electrolyses

Electrolysis at controlled potential were carried out by means of a potentiostat (Amel — 555 — SU). An equal amount of electricity (~ 2000 C), measured by electronic

integrator, was transferred during each experiment. Representative results are shown in the Table.

Preparative electrolyses were made in a jacketed water-cooled cell divided by a sintered-glass diaphragm into anode and cathode compartments. The cathode was a mercury pool (19 cm²) and the anode was a Pt-wire. A saturated calomel reference electrode was connected to the cathode compartment through a Luggin capillary.

The 0.13 M solution of acetonylacetone **1** obtained by dissolving **1** in 100 ml of catholyte (0.5 M aqueous HCl) was electrolysed at controlled potential. Temperature during electrolyses was between 18 and 20 °C. After stopping the electrolysis 20 g NaCl was added to the reaction mixture, and the mixture extracted five times with ether or ethylacetate. The combined extracts were dried (MgSO₄) and the solvent removed by distillation to a volume of 50 ml. The remaining mixture was subjected to g.l.c. analyses. Acetaldehyde, acetone and 2,5-hexanediol were identified by comparison of their respective retention times with authentic samples on at least two different chromatographic columns.

Acetic acid, 2,5-dimethyltetrahydrofuran and unreacted acetonylacetone were isolated by preparative gas chromatography and identified by comparison with authentic samples (g.l.c., n.m.r., i.r., and mass spectra).

At least three additional products whose structure has not been identified remain in the reaction mixture.

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SAŽETAK

Elektrokemijska redukcija acetonilacetona u solnoj kiselini

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Ispitana je elektrokemijska redukcija acetonilacetona na živinoj katodi u razrijeđenoj solnoj kiselini. Pokazano je da je protonirani oblik acetonilacetona 2 elektroaktivan. Eksperimentalni rezultati pokazuju da brzina elektrokemijske redukcije ovisi o prethodnom stupnju protoniranja i (ili) adsorpciji elektroaktivne vrste. Elektroliza kod kontroliranog potencijala (-1,2 V vs. S. C. E.) daje slijedeće produkte: acetaldehid, aceton, octenu kiselinu, 2,5-heksandiol i 2,5-dimetiltetrahydrofuran. Diskutiran je mehanizam nastajanja ovih produkata.

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