Electrolytic Reduction and Cleavage of Cyclohexane-1,4-dione

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The reduction of cyclohexane-1,4-dione (1), hexane-1,4-dione (2), and cyclohexanone on a mercury electrode have been investigated. Water and propan-2-ol–water (4 :1) were used as the solvents and tetraethylammonium toluene-*p*-sulphonate was the supporting electrolyte. Current–potential curves have been measured and preparative electrolyses have been performed. Only compound (1) reacted [up to −2·3 V(SCE)] and yielded the following products: 1,1'-dihydroxybicyclohexyl-4,4'-dione (3), hexane-2,5-dione (2), 4-hydroxycyclohexanone (4), and *cis*- and *trans*-1,4-cyclohexanediol [(5) and (6)]. At all potentials the yield of *cis*-compound (5) exceeded that of *trans*-compound (6). The ratio *cis* (5) : *trans* (6) decreased with increasing cathodic potential. Possible mechanistic paths leading to the different products and adsorption phenomena involved in their formation are discussed.

THE electrochemical behaviour of 1,3-diketones has been reported to be affected by intramolecular interaction between the carbonyl functions.[1-3] These compounds, even when C-2 was disubstituted to avoid enolisation, reduced at less negative potentials than the corresponding monoketones.[3d] In the reaction mixtures cyclopropane derivatives and rearranged products [1,3c] resulting from the latter could be detected. The research on intramolecular interaction between carbonyl groups during electroreduction has now been further extended to the study of 1,4-diketones.

The cyclic 1,4-diketone (1) and its open-chain analogue (2) were chosen as representative compounds and their behaviour was compared to that of cyclohexanone. Of the three compounds tested, only (1) could be reduced electrochemically under the experimental conditions prevailing, up to the highest negative potential employed (−2·3 V). Current–potential curves measured on solutions of (2) or cyclohexanone could not be distinguished experimentally from the background currents of the appropriate electrolytes. Preparative electrolysis of solutions containing (2) or cyclohexanone at −2·3 V yielded no products and the reactants were quantitatively recovered. Thus, the results given below pertain to compound (1) only.

Current–potential curves for several concentrations of (1) in 0·5M-aqueous solution of tetraethylammonium toluene-*p*-sulphonate (Et_4N *p*-Ts) are presented in Figure 1. It is noted that the curves corresponding to concentrations above 0·08M (1) coincide, indicating saturation of the electrode surface by the reactant molecule and/or intermediates formed in the reduction sequence.[3b]

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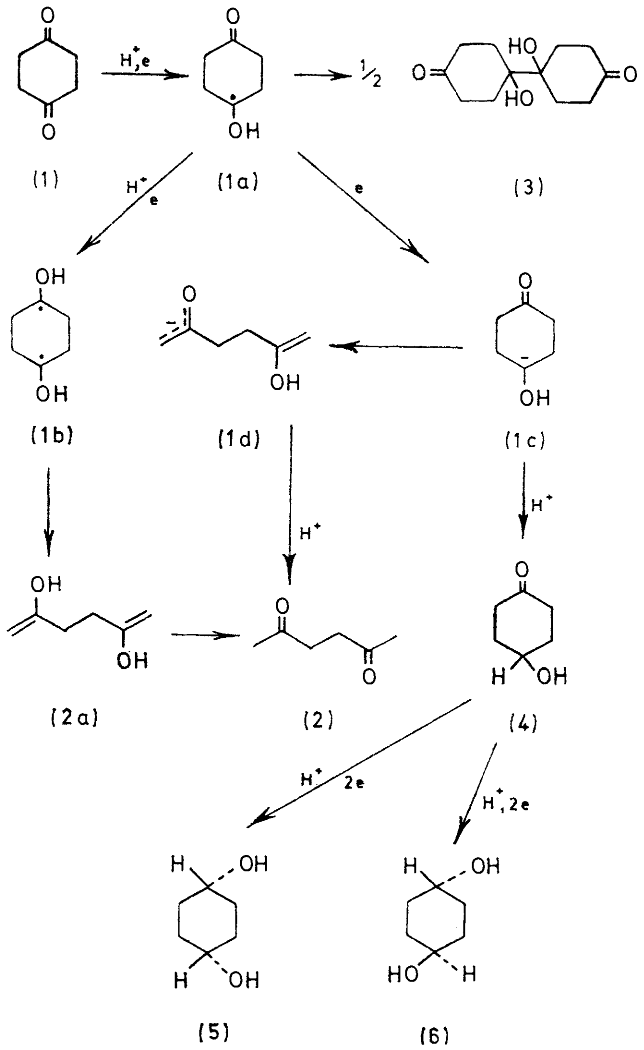
[1] T. J. Curphey, C. W. Amelotti, T. P. Layloff, R. L. McCartney, and J. H. Williams, *J. Amer. Chem. Soc.*, 1969, **91**, 2817.

[2] D. H. Evans and E. C. Woodbury, *J. Org. Chem.*, 1967, **32**, 2158; R. C. Buchta, and D. H. Evans, *Analyt. Chem.*, 1968, **40**, 2181; *J. Electrochem. Soc.*, 1970, **117**, 1494; *J. Org. Chem.*, 1970, **35**, 2844.

[3] (*a*) E. Kariv, J. Hermolin, and E. Gileadi, *J. Electrochem. Soc.*, 1970, **117**, 342; (*b*) *Electrochim. Acta*, 1971, **16**, 1453; (*c*) E. Kariv, B. J. Cohen, and E. Gileadi, *Tetrahedron*, 1971, **27**, 805; (*d*) E. Kariv, J. Hermolin, I. Rubinstein, and E. Gileadi, *ibid.*, p. 1303.

In some experiments water was replaced by a mixture of propan-2-ol–water as the solvent. The reaction products were the same in both solvents, but lower reduction currents and a markedly higher background current were found in the propan-2-ol–water system (Figure 2). Hence, all further experiments were performed in pure water.



SCHEME

The electrolysis products (2)—(6) were isolated and identified. Their yields are shown in the Table as a function of current-density and potential. Plausible, parallel and consecutive steps in the reaction pathway are shown in the Scheme.

The first step in the reduction is the addition of an electron and a proton to (1) to form the radical (1a). This can dimerise to the pinacol (3) in an overall reaction similar to that found in the reduction of dimedone.[3a,b] The same product (3) could be obtained by further reduction of (1a) to the anion (1c) and combination with a reactant molecule (1). This mechanism, however, has been shown [3b] to be inconsistent with experimental results in the case of dimedone and is unlikely to be predominant in the present system.

The product (2) is rather unusual in that it must be formed by the cleavage of a C–C bond of the cyclic reactant (1), while the two carbonyl functions apparently remain intact. The direct electrolytic fission of such bonds is not known to occur in the potential range studied here. A reasonable path to this product (2) is through biradical (1b) formed by one-electron addition to (1a). The biradical (1b) upon rearrangement yields the dienol (2a), isolated as its stable diketonic tautomer (2). A similar mechanism was recently proposed [4] for the reductive cleavage of (1) to (2) with amalgamated zinc in hydrochloric acid. Alternatively, the fragmentation of (1) may involve the break-up of (1c) to the delocalised anion (1d). Protonation of this intermediate would give rise to the diketone (2).

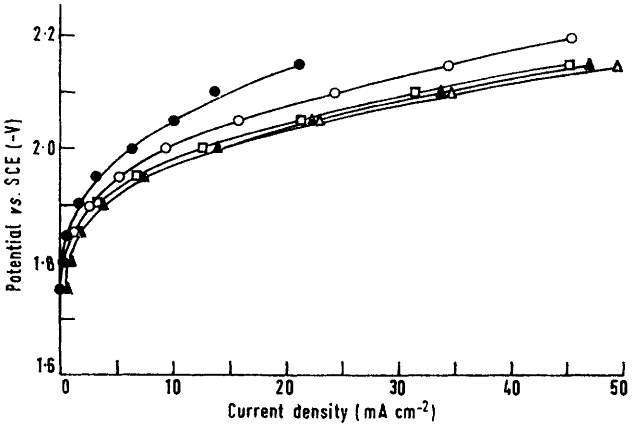


FIGURE 1 Current–potential curves for the reduction of (1) in 0·5M-aqueous Et_4N *p*-Ts; ● = 0·01M; ○ = 0·02M; □ = 0·04M; ▲ = 0·06M; △ = 0·08 and 0·12M

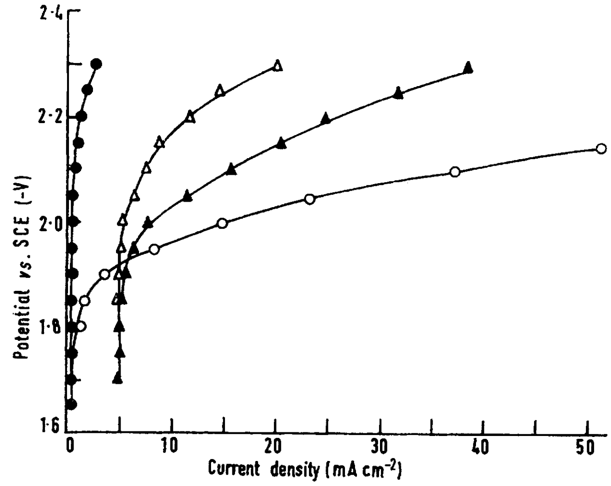


FIGURE 2 Current–potential curves in 0·5M-Et_4N *p*-Ts for: ● = electrolyte in water; △ = electrolyte in propan-2-ol–water (4 : 1); ▲ = 0·12M-(1) in propan-2-ol–water (4 : 1); ○ = 0·12M-(1) in water

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[4] E. Wenkert and J. E. Yoder, *J. Org. Chem.*, 1970, **35**, 2986.

The hydroxy-ketone (4) is probably the protonation product of the anion (1c). It is interesting to note that (4), although it has a single keto-group, was reduced in the same potential region as the diketone (1). Under identical conditions cyclohexanone was unreactive, which indicates that the hydroxy-group in the γ-position enhances the reactivity of the carbonyl function of (4).

The diols (5) and (6) could have been formed by two-electron transfer (direct or two consecutive one electron steps) to the reduction product (4). They are the only reaction products which have a potential-dependent yield (see Table). Moreover, the ratio *cis* (5) to *trans* (6) is 8 : 1 when electrolysis is carried out at −1·95 V and decreases by a factor of *ca.* 3 as the potential is −2·10 V. Even more intriguing is the fact that electrolysis of the hydroxy-ketone (4) at the above potentials also yields the diols (5) and (6), but now in equal amounts of the *cis*- and the *trans*-isomers. These experimental results indicate that two different mechanisms are involved in the formation of the diols from (4) and (1).

Composition of the reaction mixtures obtained by electrolysis of 0·18M-compound (1) in aqueous solution ($0·5M-Et_4N$ *p*-Ts)

Current-density mA cm^{-2}	Potential (V) (SCE)	Time (h)	(1) %	(3) %	(2) %	(4) %	(5) and (6) %	*cis* (5) : *trans* (6)
2·56	1·95	4	62	6·5	9	19	0·6	8 : 1
5·13	2·00	2	63	6	9	18	0·9	4 : 1
10·26	2·05	1	63·5	5·5	9	17	1·1	3 : 1
20·52	2·10	1/2	64	5	9	17	1·3	2·5 : 1

It may be suggested that at least part of the intermediates participating in the reduction of (1) are adsorbed on the surface until four electrons have been transferred to form the diol. It has been shown[5] that the diketone (1) exists as an equilibrium mixture of chair and boat forms. The boat conformations probably have a higher energy of adsorption than the chair conformations since they allow overlap of the π orbitals of both carbonyls with the surface energy states of the metal. The same applies to the conformation of the adsorbed radical intermediate (1a) * which again will be more stable in the boat conformation due to interaction of the *p* and π orbitals with the cathode surface. It is apparent that further reduction and protonation of the adsorbed intermediates in the boat form would lead to the *cis*-diol (5) rather than to the *trans* (6). On the other hand, if the species being reduced are dissolved in the solution (in either conformation) they are expected to yield a mixture of *cis*- and *trans*-isomers since protonation may occur now from either side of the carbocyclic ring. The fact that reduction of (4) yields a mixture of 1 : 1 of (5) and (6) indicates that the rates of protonation from either side of the ring system are equivalent for an intermediate which is either bound to the electrode at one site only or free in the bulk.

The potential dependence of the ratio of products (5) and (6) starting from (1) is consistent with the explanation given above. Reduction of (1) takes place at high negative rational potentials,† *i.e.* at potentials which are cathodic with respect to the potential of zero charge in this system. It is well known[7] that adsorption of organic species is highest in the vicinity of the potential of zero charge and decreases with increasing rational potential. Thus as the potential is changed from −1·9 to −2·10 V the surface concentration of intermediates decreases. If one assumes that reduction of an adsorbed intermediate yields the *cis*-isomer (5) while reduction of the same species in solution leads to a nearly equal mixture of *cis*- and *trans*-isomers, the decrease of the ratio *cis*- to *trans*-isomers formed with increasing potential is directly predicted.

To conclude, the 1,4-diketone (1) is reduced at less-negative potentials than required for the reduction of cyclohexanone, evidently due to the presence of the second carbonyl group in the molecule. The exact nature of the effect of the second carbonyl group at C-4 of (1) is not fully understood and will be further investigated. It is noteworthy that (4) which is a monoketone and has a hydroxy-group at C-4 is reduced in the same potential range as (1). A similar effect could not be observed for the acyclic 1,4-diketone (2). The main difference between (1) and (2) is the relative position of the carbonyl groups in the stable conformation of their molecules. Thus, the spatial relationship between the electroactive groups is a determining factor for both the rates of reaction and the stereochemical consequences. Evidence for a 1,4-interaction during the electrochemical reduction of (1) was obtained by isolation of the ring-cleaved product (2).

EXPERIMENTAL

Materials and Purification Methods.—Mercury (Merck G.R. and for polarography) was filtered and redistilled before use. Propan-2-ol was purified[8] by distillation over $NaBH_4$ and Mg under nitrogen. Double-distilled water was used and the nitrogen purified from traces of organic and reducible substances. Tetraethylammonium toluene-*p*-sulphonate[9] (Et_4N *p*-Ts) was prepared from ethyl toluene-*p*-sulphonate and triethylamine; it was recrystallised from ethanol–ether and dried *in vacuo* over

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* The radical (1a) is probably chemisorbed on the surface and may be regarded as an equivalent to an organo-mercury surface compound, which has been postulated[6] as a possible intermediate in the reduction of ketones.

† The rational potential is defined as the potential with respect to the potential of zero charge in the same system $\hat{E} = E - E_{pzc}$.

[5] A. Aihara and C. Kiatzawa, *Bull. Chem. Soc. Japan*, 1971, **44**, 99.

[6] J. P. Coleman, R. J. Kobylecki, and J. H. P. Utley, *Chem. Comm.*, 1971, 104.

[7] J. O'M. Bockris, E. Gileadi, and K. Müller, *Electrochim. Acta*, 1967, **12**, 1301; E. Gileadi, *J. Electroanalyt. Chem.*, 1966, **11**, 137.

[8] B. E. Conway, E. J. Rudd, and L. G. M. Gordon, *Discuss. Faraday Soc.*, 1968, **45**, 87.

[9] M. M. Baizer, *J. Electrochem. Soc.*, 1964, **111**, 215.

P_2O_5. Cyclohexane-1,4-dione (1) (Fluka puriss) was purified by sublimation *in vacuo*. Hexane-2,5-dione (2) and cyclohexanone (B.D.H.) were distilled under reduced pressure and used immediately.

Electrical Measurements and Preparative Electrolyses.—A dropping-mercury electrode from a fine polarographic capillary served as the working electrode. The drops were knocked off every 0·24 s by means of an electromechanical timing device (Metrohm, A.G. Herisau, Schweiz, E-354 polarographic stand). The maximum drop-size ($3{\cdot}24 \times 10^{-3}$ cm^2) was calculated by weighing all the drops collected in 10 min and assuming a hemispherical shape.[3b] A commercial saturated calomel electrode (Radiometer, K-401) was used as a reference and a platinised platinum foil served as the counter electrode. All potentials reported are *vs.* this reference electrode.

Current–potential measurements were performed potentiostatically (Elron, CHP-1 potentiostat). The potential was varied linearly with time, at a rate of 1 mV s^{-1} by means of a function generator (Elron, CHF-1). Current–potential curves were plotted on an X–Y recorder (Moseley 7030 AM). Maximum currents were measured at each potential, corresponding to maximum drop size, just before the drop was knocked off. Nitrogen was bubbled through the solution before each measurement and over it during the measurement.

Measurements and preparative electrolyses were carried out in water and propan-2-ol–water (4 : 1) with 0·5M-Et_4N *p*-Ts as the electrolyte. Pure water was a more convenient solvent for experimental purposes because of its low background current (Figure 2). However, propan-2-ol–water solutions had to be used, in order to avoid solubility problems during the comparison of the electrochemical behaviour of compounds (1) and (2) and cyclohexanone. Studies on the composition of the reaction mixtures of (1), obtained in both media, showed no solvent effect on the products and their yields.

Preparative electrolyses were performed galvanostatically, with a galvanostat Elron CHG-1, in large cells with a mercury pool (19·5 cm^2) cathode. The counter electrode (platinised platinum foil) was enclosed in an Alundum tube, dipping into the solution and the reference electrode was brought within 1 mm from the surface of the mercury pool. The substance to be reduced was introduced only into the cathode compartment. Nitrogen was bubbled during electrolysis, and the solution was mechanically stirred.

Steady-state current–potential curves measured under identical experimental conditions as the preparative electrolyses were similar to those obtained with the dropping mercury electrode.

I.r. spectra were recorded on a Perkin-Elmer Infracord-337. N.m.r. spectra were run with a Varian HA 100 and mass spectra were obtained with an Atlas CH_4. G.l.c. was performed on a Varian Aerograph 1800 on 5% sorbitol on Chromosorb W, AW 60/80 ($\frac{1}{4}$ in × 7 ft) and 10% Carbowax 20M on Chromosorb W, AW 60/80 ($\frac{1}{4}$ in × 5 ft) columns.

Electrolysis of Cyclohexane-1,4-*dione* (1).—Several electrolyses were carried out at each of four potentials, an equal amount of charge being transferred during every experiment. Representative results are shown in the Table.

A 0·18M-solution obtained by dissolving (1) (2 g) in 0·5M-aqueous Et_4N *p*-Ts (100 ml) was electrolysed. Extensive darkening, which occurred at room temperature, was avoided by performing the experiment at 1 °C. After the electrolysis was stopped, NaCl (25 g) was added (with stirring and cooling in an ice-bath) and the mixture was repeatedly extracted with ethyl acetate. The combined ethyl acetate fractions were dried ($MgSO_4$) and the solvent was removed at room temperature under reduced pressure. The remaining residue was chromatographed on silica (Merck, 0·05—0·20 mm) and was found to consist of the following compounds: hexane-2,5-dione (2) which was identified by comparison with an authentic sample by means of g.l.c., n.m.r., and i.r. spectra. The pinacol (3), m.p. 145° (corr.), $\nu_{max.}$ (KBr) 3370 (OH) and 1700 (C=O) cm^{-1}; δ [$(CD_3)_2CO$] 1·5—2·5 (m) p.p.m. [the n.m.r. spectrum of (3) in D_2O resembles that of (4) in the same solvent except for the proton adjacent to the OH group which appears as a multiplet at δ −4·3 p.p.m.], *m/e* 224(*M* − 2), 113(*M*/2), and 112(*M*/2—1).

The hydroxy-ketone (4)[10] was identified by comparison with a synthetic sample (g.l.c., n.m.r., and i.r.). *cis*- and *trans*-1,4-Dihydroxycyclohexanone (5) and (6)[11] were identified by comparison (g.l.c., n.m.r., and i.r.) with commercial samples (B.D.H.). The two isomers could not be separated either by chromatography on silica or g.l.c. on SE-30, Carbowax 20M, hyprose, diethylene glycol succinate, and Apiezon L columns. Finally, separation was achieved by g.l.c. on a sorbitol column. A small fraction (2—3%) of unidentified mixture was also isolated. It probably consisted of dimeric products resulting from further reduction of (3). This fraction had an intense OH band a weak C=O band in its i.r. spectrum. Its mass spectrum measured at a low ion source potential (0·3 eV) displayed molecular peaks in agreement with the proposed assumption; *m/e* 228, 226, 224, and 112.

Synthesis of 4-*Hydroxycyclohexanone* (4).—The reported[10] synthesis of (4) gave poor yields and better results were obtained by the following method. An ice-cold solution of potassium dichromate (6 g) in sulphuric acid (6 ml) and water (100 ml) was added to 1,4-dihydroxycyclohexane (7 g) previously dissolved in water (100 ml). After being stirred overnight at room temperature followed by neutralisation with aqueous sodium hydrogen carbonate the reaction mixture was repeatedly extracted with ethyl acetate. The organic layer was dried ($MgSO_4$) and the solvent was removed. The remaining oil was chromatographed on a silica (Merck) column and found to consist of (1) (14%), (4) (72%), and starting material (14%).

Electrolysis of Compound (2) *and Cyclohexanone.*—Both compound (2) and cyclohexanone were quantitatively recovered after being exposed to electrolysis at −2·3 V under identical conditions as those applied for the electrolytic reduction of (1).

Electrolysis of 4-*Hydroxycyclohexanone* (4).—Under identical conditions as those described for (1) at a potential of −2·10 V (4) yielded compounds (5) and (6) and some unchanged starting material. The ratio *cis* (5) to *trans* (6) was found to be 1·0. The electrolytic reduction of (4) was repeated several times to avoid erroneous results.

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