THE REDUCTION OF β-DIKETONES ON MERCURY

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The electroreduction of enolisable and non-enolisable β-diketones has been investigated and compared to the reduction of α,β-unsaturated and saturated ketones (for four model compounds). An explanation for the distribution of products and a mechanism for their formation are suggested.

The electroreduction of ketones on mercury has been extensively studied[1-13]. The carbonyl group can be reduced more easily when conjugated to an unsaturated center[1,13-17]. The products of reduction are either pinacols or the corresponding alcohols (or both). Transfer of one electron per molecule leads to the formation of radicals which dimerise to the pinacol. This is favoured by high pH and low cathodic potentials. At higher potentials and in acid media the radical is further reduced to the anion. This, followed by abstraction of a proton from the solvent, leads to the corresponding alcohol[2-4,12,13,16]. Polarographic reductions[14,15,18-22] and some preparative electrolyses[19,23,24] of β-diketones have been reported.

The purpose of the present investigation was to correlate the reducibility of two representative β-diketones *II* and *III* with their structure, to identify the products, determine the reaction mechanism and rationalise the distribution of products found.

EXPERIMENTAL

Materials and Cleaning Procedures

Cyclohexanone (*I*) (B.D.H., R.G.) was redistilled before use. 2,2,5,5-Tetramethyl-1,3-cyclo-hexadione (*II*)[25] was prepared by methylation of *III* and purified by repeated recrystallisations from n-pentane. 5,5-Dimethyl-1,3-cyclohexadione (*III*) (Fluka *puriss.*) was recrystallised from methanol–water. 5,5-Dimethyl-2-cyclohexenone (*IV*) was synthesised by LiAlH₄ reduction[26]

from 3-methoxy-5,5-dimethyl-2-cyclohexenone[27]. The purity of all the compounds was checked by VPC, TLC and NMR Mercury (Merk GR and for polarography) was filtered and redistilled before use. 2-Propanol was purified by distillation over $NaBH_4$ and Mg under nitrogen[10]. Triple distilled water was used and the nitrogen bubbled through the cell was purified from traces of organic and reducible substances. Tetraethylammonium p-toluenesulfonate[28] was prepared from ethyl p-toluenesulfonate and triethyl amine, recrystallised from ethanol–ether mixtures and dried under vacuum over phosphorus pentoxide.

Electrodes

A dropping mercury electrode from a fine polarographic capillary served as the working electrode. The drops were knocked off every 0·20 seconds by means of an electrochemical timing device (Metrohm, A.G. Herisau, Schweiz, E-354 polarograph stand). The maximum drop-size was calculated by weighing all the drops collected in 10 minutes and assuming a hemispherical shape. A commercial saturated calomel electrode (Radiometer type K 401) was used as reference and a platinized platinum foil served as the counter electrode. All potentials reported are vs. this reference electrode.

Electrical Measurements

Current–potential measurements were carried out potentiostatically in 0·5M tetraethylammonium-p-toluenesulfonate in 2-propanol–water (4 : 1) using an Elron model CHP-1 potentiostat. The potential was varied linearly with time, at a rate of 3 mV/s. (Elron model CHF-1 function generator). Current–potential curves were plotted on an X–Y recorder (Moseley model 7030 AM). Maximum currents were measured at each potential, corresponding to maximum drop size, just before the drop is knocked off.

RESULTS AND DISCUSSION

REDUCIBILITY OF KETONES

The ease of reduction of ketones is judged by two criteria, a) the initial reduction potential E_i, which is determined by extrapolating the current–potential curve to zero current (cf. Fig. 1); b) the reaction limiting current. The initial reduction potential E_i is used instead of the half-wave potential $E_{1/2}$ because the reactions studied are highly irreversible and $E_{1/2}$ is poorly defined.

Several groups of saturated ketones, β-diketones and α,β-unsaturated ketones were studied[29]. For a typical series shown below the reactivity increased from I to IV as shown in Figs 1 and 2. The curves in these figures correspond to surface saturation by an adsorbed species. This is confirmed by the fact that further increase in concentration does not alter rate of reaction as shown in Fig. 3 for the case of the αβ unsaturated ketone IV. Thus the limiting current observed in Fig. 2 should be considered as a reaction limited current (as discussed in detail elsewhere[30]). The reduction of cyclohexanone (I) could not be achieved under these experimental conditions (this is why no curve for I is presented). On the other hand the reduction of the cyclohexenone IV was relatively easy. This is due to the stabilization of the radical inter-

I   *II*   *III*   *IV*
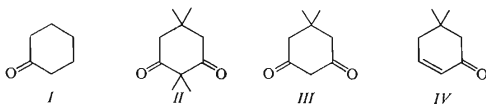
mediate *IVa* formed by electroreduction[13-17]. The reduction of the enolisable
β-diketone *III* proceeds at almost the same rate as that of *IV*, their $E_{\frac{1}{2}}$ values and
limiting currents differing only slightly (Fig. 2). The difference in the electrochemical
behaviour of *I* and *III* and the similarity of *III* and *IV* can be explained by the as-
sumption that the enolic form of *III* is the reactive species on the electrode. This
will allow the formation of a stabilized radical *IIIa* of the same type as *IVa*.
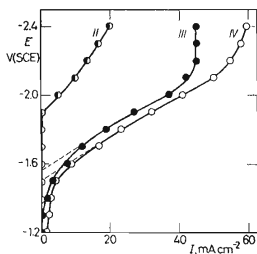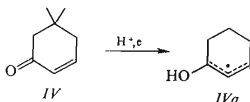

IV $\xrightarrow{\text{H}^+,\text{e}}$ *IVa*

Fig. 1

Saturation Current–Potential Plots for the
Reduction of 5,5-Dimethyl-2-cyclohexenone
(*IV*) (0·7 and 0·9M), 5,5-Dimethyl-1,3-cyclo-
hexadione (*III*) (0·8 and 1·0M) and 2,2,5,5-
Tetramethyl-1,3-cyclohexadione(*II*) (0·22 and
0·4M);

0·5M tetraethylammonium-*p*-toluenesulfo-
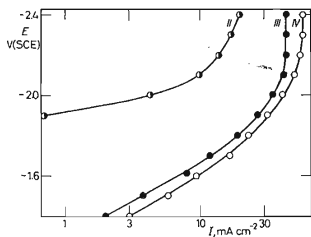nate in 2-propanol–water 4 : 1, corrected for
background.

Fig. 2

Saturation Current–Potential Plots on a Semi-
log. Scale

Substrates and conditions the same as
in Fig. 1.

The non enolisable β-diketone *II* is less readily reduced than the enolisable β-diketone *III* but it is still more reactive than the saturated ketone *I* (Figs 1 and 2). This can be attributed to a homoallylic delocalization in the radical *IIa*.


III   *IIIa*
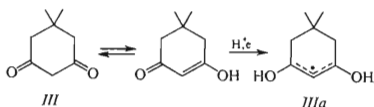
Homoallylic conjugation in β,γ-unsaturated ketones was encountered in studies of their UV spectra[31,32]. Homoallylic interaction is well known for carbonium ions[33], carbanions[34] and it had also been observed in radicals[35].

PRODUCTS DISTRIBUTION

The products from the electroreduction of *III*, *IV* and *II* have been isolated and identified. The reduction of the enolisable β-diketone *III* yields only the dimer *V*[24,30], independent of the potential applied. The same type of products is obtained from the


II   *IIa*
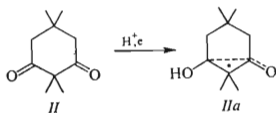
reduction of *IV*[36-37]. On the other hand, the reduction of the nonenolisable β-diketone *II* yields the dimer *VI* and the monomeric alcohol *VII*. The ratio monomer–dimer increases with increasing negative potential. This behaviour strongly suggests that the monomer *VII* is a product of an additional electron transfer to the radical *IIa* formed initially. Production of the dimer *VI* and the monomer *VII* are then competing parallel reactions. Since the rate of the latter is potential dependent while that

IIIa ⟶

V
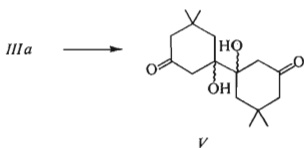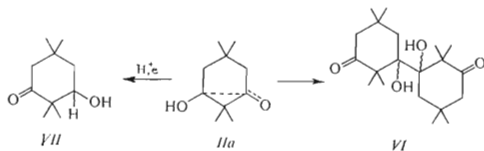
of the former is not,* an increase in the ratio of monomer to dimer with increasing potential is expected. The unique behaviour of the nonenolisable diketone *II* as compared to the two other compounds tested (*III* and *IV*) both with respect to ease of reduction and product formation can be explained in terms of the stability of the radical intermediate formed. The radical *IIa* is least stable of the three while the stability of *IIIa* and *IVa* is nearly the same. Thus *IIIa* and *IVa* are more readily formed (*i.e.* the ketones *III* and *IV* can be reduced at a lower potential) but once formed it is difficult to reduce them further. Conversely, *IIa* is formed with greater difficulty (at higher cathodic potential) but it can be further reduced more readily. The more stable radicals form the dimer while the less stable radical yields a mixture of the dimer and the monomer.
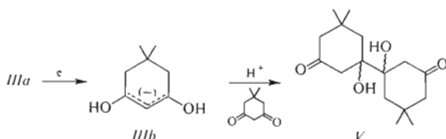

THE ELECTROCHEMICAL MECHANISM

The mechanism of reduction of the enolizable β-diketone *III* has been discussed in detail recently[30]. A similar mechanism for the α,β-unsaturated ketone *IV* has not been proposed in the literature, but in view of the similarity of products and of the current–potential curves (Fig. 3 *vs.* Fig. 4) it is rather likely that the same mechanism is operative. The case of compound *II* is rather more complex. The range of potential

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*   It may be argued that the rate of formation of the dimer *VI* is also potential-dependent, due to the potential dependence of the surface concentration of its precursor[38–39]. It was argued elsewhere[30] that in the relevant potential region the surface concentration decreases with increasing cathodic potential. Thus if the rate of formation of the dimer depends on the square of the surface concentration of the intermediate, while the rate of formation of the monomer depends on the first power of this concentration, the ratio monomer–dimer would increase even further with increasing cathodic potential.

available for experimental study is much narrower (*cf.* Figs 1,2) and even in this range two products are formed with their ratio varying with potential. Thus the electrochemical mechanism of reduction of compound *II* could not be determined with certainty, although some indications are available, as will be discussed below.

The following mechanism can be proposed for the reduction of *III* (ref.[30]):
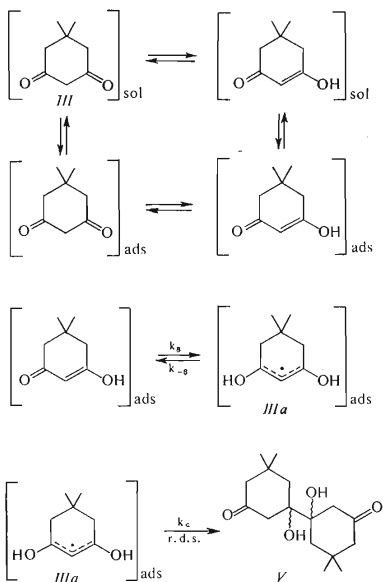
The four equilibria in step (*A*) simply indicate that the enolic form adsorbed on the surface is at equilibrium with the reactant *III* in solution either through the enolic form in solution or through the adsorbed reactant itself. The charge transfer step (*B*) is fast and at quasi-equilibrium, followed by a surface recombination rate-determining step (*C*). Three major experimental observations lead to the proposition of the above mechanism: *a*) The product of the reaction has been analysed as the dimer *V*. *b*) The observed current density becomes independent of concentration beyond 0·8M at all potentials (*cf.* Fig. 4). *c*) A reaction limited current is observed at potentials above −2·0 V (s.c.e.). (*cf.* Fig. 4.).

For the mechanism proposed the current density is given by

$$i = nFk_C\Theta_{IIIa}^2, \qquad (1)$$

where Θ_{IIIa} is the fractional surface coverage by the radical $IIIa$. This equation leads to a reaction limited current, independent of concentration and of potential, when $\Theta_{IIIa} \to 1$, as observed at high potentials (*cf.* Fig. 4).

Charge transfer occurs between two adsorbed species (step (B)). The ration of their respective surface coverages may be expressed as

$$\Theta_{IIIa}/\Theta_{III} = K_B c_{H^+} \exp\left(-\Delta\Phi F/RT\right), \qquad (2)$$

where Θ_{III} is the fractional surface coverage by the adsorbed enolic form of the diketone III and $K_B = k_B/k_{-B}$. Further, one can relate Θ_{III} to C_{III}. the concentration in solution, by the equation

$$\frac{\Theta_{III}}{1 - \Theta_t} = Kc_{III}, \qquad (3)$$

where K is a composite constant taking into account all the equilibria in step (A) and $\Theta_t = \Theta_{III} + \Theta_{IIIa}$. At high concentration and low (*i.e.* less cathodic) potentials
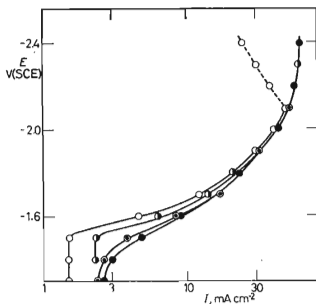

FIG. 3

Current–Potential Plots for the Reduction of 5,5-Dimethyl-2-cyclohexenone (IV)

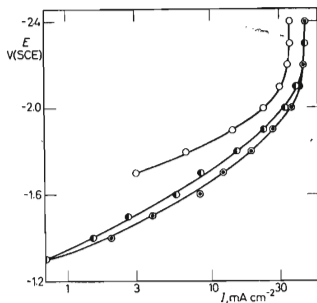○ 0·1M, ◑0·2M, ⊙ 0·5M, ● 0·7 and conditions the same as in Fig. 1.

FIG. 4

Current–Potential Plots for the Reduction of 5,5-Dimethyl-1,3-cyclohexadione (III)

○ 0·2M, ◑ 0·5M, ⊙ 0·8 and 1M; conditions the same as in Fig. 1.

Θ_{III} approaches unity and Θ_{IIIa} is very small. Combination of equations (1), (2) and (3) shows that under these conditions the current density becomes independent of concentration, yet it depends on potential due to the equilibrium in step (B). Such behaviour is shown experimentally in Fig. 4. The detailed kinetic equations relevant to this mechanism have been derived elsewhere[30].

An alternative mechanism has been proposed[30] leading to the same product. This involves a second charge transfer, but the resulting anion IIIb combines with a neutral reactant molecule to form the dimer V.

This mechanism has been analysed in detail[30] and shown to be inconsistent with experiment. This conclusion is also indicated by consideration of the products formed. Thus, if the radical IIIa could be easily reduced to form the anion IIIb, it would be difficult to see why some of these anions do not abstract a proton from the solvent to form the monoalcohol analogous to VII under essentially identical conditions. As stated above, the monoalcohol could not be detected in the products of reduction of III or IV.

The information on the kinetics of reduction of II is somewhat more limited, as pointed out above. Nevertheless, it has been established[40] that the current density becomes independent of concentration, indicating that an adsorbed species takes part in the rate determining step. At lower potentials, where the dimer VI is predominantly formed, the mechanism is probably the same as that of III and IV. At high cathodic potential a clear limiting current could not be observed, (Figs 1, 2) although in a series of similar diketones[29] such a limiting current region was observed. This mechanism will be discussed in greater detail elsewhere[40].

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