

ELECTROREDUCTION OF 1,3-DIKETONES AND SOME OF THEIR 2,2-DISUBSTITUTED DERIVATIVES

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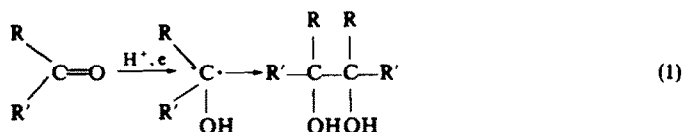
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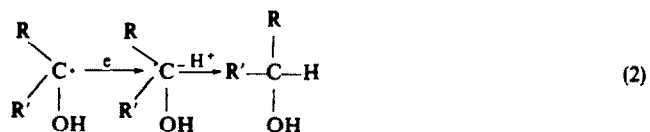
Abstract—The electroreduction of four representative 1,3-diketones and their 2,2-disubstituted derivatives on a mercury electrode was investigated. Current/potential curves of similar shape were obtained in each case, becoming independent of concentration at higher concentrations. An initial reduction potential $-E_i$ was determined by extrapolating the current/potential curves, in the high concentration region, to zero current density. This quantity was used as a measure of the reactivity of the compounds tested towards reduction. The reactivity was correlated with the structure of the diketone and the radical formed from it by charge transfer.

INTRODUCTION

THE electroreduction of ketones in protic media¹⁻⁸ proceeds through the addition of a proton and an electron, forming a radical (Eq. 1).



This radical can form the corresponding pinacol by dimerization (Eq. 1). Alternatively, if the potential is sufficiently cathodic, a second charge-transfer may occur. The anion thus formed yields the alcohol by abstraction of a proton from solution (Eq. 2)



It was noted that conjugation in the ketone molecule shifts the reduction potential for both reactions (1) and (2) to less negative values, implying that the energy of activation for these processes is decreased.

The purpose of our investigation was to study the mutual effect of the carbonyl functions of 1,3-diketones on their electrochemical behaviour.*

RESULTS AND DISCUSSION

Current/potential curves at different concentrations were measured for the compounds listed in Table 1. All the compounds except the saturated ketones I, VII, X

* Some polarographic data^{9,10,13-17} and some preparative electrolyses^{14,18,19} of such compounds have been previously reported.

and XI behaved similarly and exhibited at higher concentrations, current/potential curves which are independent of concentration. Fig 1 shows a typical set of current/potential curves over a wide range of concentrations, for the case of 2-acetylcyclohexane-1-one (VI). The lack of concentration dependence implies zero order kinetics, probably due to saturation of the surface by adsorbed species.¹⁹ The values of E_i in Table 1 were derived from the saturation curves by extrapolation to zero current density. In all further figures in this paper only the saturation curves are given for each compound.

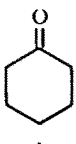
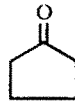
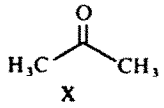
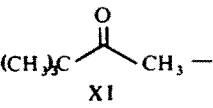
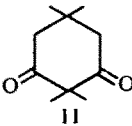
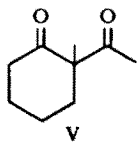
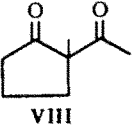
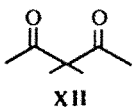
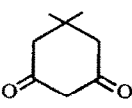
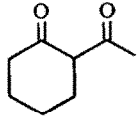
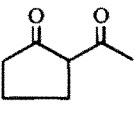
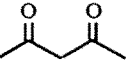
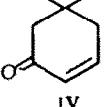

The initial reduction potential E_i was used to compare the electrochemical reactivity of the different compounds; a more negative value of E_i indicating a higher energy of activation for reduction.

In Figs 2, 3, 4 and 5, saturation curves are plotted for four series of compounds each consisting of a saturated ketone and two related 1,3-diketones one with a disubstituted 2-carbon and one with an unsubstituted 2-carbon (Table 1). In addition the α,β -unsaturated ketones IV and XIV, belonging to the series A and D respectively, were also examined.

Comparison of the E_i values within each series shows the following decreasing order of reactivity:

α,β -unsaturated ketone > 2-unsubstituted 1,3-diketone > 2,2-disubstituted-1,3-diketone > saturated ketone.

TABLE 1. LIST OF COMPOUNDS TESTED WITH THEIR RESPECTIVE "INITIAL REDUCTION POTENTIALS"— E_i

Ser A	E_i (V)	Ser B	E_i (V)	Ser C	E_i (V)	Ser D	E_i (V)
	—	—	—		—		—
							—
	1.90		1.86		1.77		1.88
	1.61		1.57		1.51		1.68
	1.55						1.32

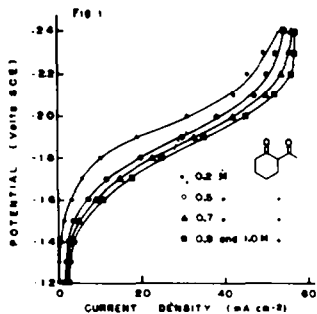


FIG 1. Current/potential curves for the reduction of VI corrected for background current

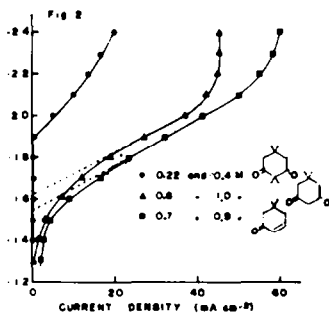


FIG 2. Saturation current/potential curves for the reduction of II, III, and IV (ser. A), corrected for b.g.

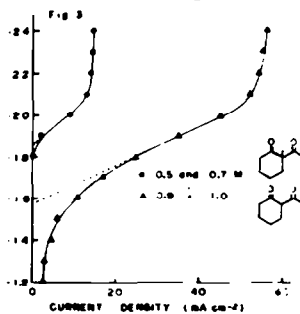


FIG 3. Saturation current/potential curves for the reduction of V and VI (ser. B), corrected for b.g.

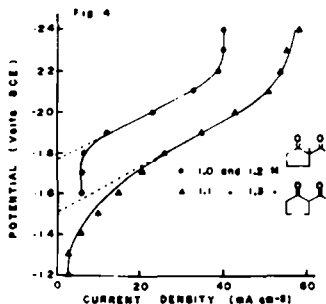


FIG 4. Saturation current/potential curves for the reduction of VIII and IX (ser. C), corrected for b.g.

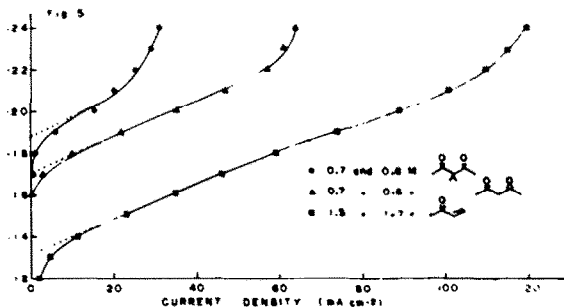
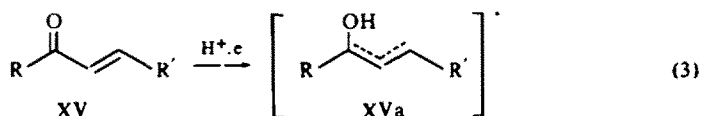
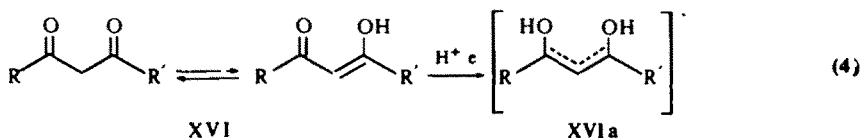


FIG 5. Saturation current/potential curves for the reduction of XII, XIII and XIV (ser. D) corrected for b.g.

The reduction of the saturated ketones I, VII, X and XI could not be achieved at potentials up to -2.4 V S.C.E. The least negative E_i values were obtained for the α,β -unsaturated ketones IV and XIV (Table 1). Their comparatively high reactivity has been previously attributed to the ability of the α,β -unsaturated radical XVa to distribute the extra electron added over a larger region than would be possible for a saturated radical^{1,7-12} (Eq. 3).



The 1,3-diketones III, VI, IX and XIII are in equilibrium with their enolic form which would, upon reduction, give rise to a relatively stable radical XVIa similar to XVa (Eq. 4). As a consequence they would be more reactive than the saturated ketones as was indeed confirmed experimentally (Table 1).

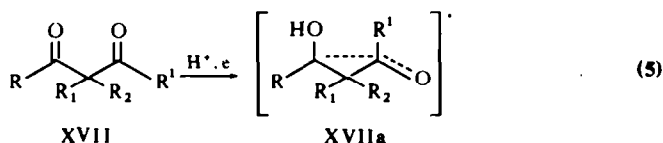


It may be argued that the radical XVIa is somewhat more stable than the radical XVa because of participation of the second hydroxyl in distribution of the extra electron. However, the E_i values measured are more negative for 1,3-diketones than for the corresponding α,β -unsaturated ketones. Since 1,3 diketones do not exist only in their enolic form under these experimental conditions (alcohol water solution) it is possible that both ketone and enol reach the electrode. The enol is the only one that reacts but the effective area of the electrode available for reaction is diminished by the presence of the ketone.

The differences in E_i values between III and IV (60 mV) on the one hand and between XIII and XIV (360 mV) on the other hand, are in accord with this hypothesis. The cyclic 1,3-diketones are almost completely enolised in alcohol/water solution while the acyclic ones exist in a larger part in their ketonic form.²⁰

The dependence of E_i on the keto-enol equilibrium may be used as a measure of the degree of enolization of ketones.

The reduction of the 2,2-disubstituted-1,3-diketones II, V, VIII and XII was achieved at less negative potentials than the reduction of the respective saturated ketones I, VII, X and XI. Since allylic conjugation in the radical XVIIIa is not possible, the shift in the E_i value may be attributed to homoallylic distribution of the extra electron in XVIIa (Eq. 5).



The values of E_i measured for the 2,2-disubstituted-1,3-diketones II, V, VIII and XII were more negative than those measured for the corresponding 2-unsubstituted 1,3-diketones III, VI, IX and XIII respectively, by 0.20–0.29 V, difference in energy of 4.6–6.7 Kcal/mol (a difference of 1 V in the reduction potential corresponds to 23 Kcal/mol for the transfer of one electron per molecule). This difference is probably due to the better allylic stabilization in radical XVIa as compared to the homoallylic stabilization in radical XVIIa.

Homoallylic interaction in radicals has been previously reported.²¹ Such interactions have been observed also in *two electron* reductions of 1,3-diketones during electrochemical,¹⁸ Clemmensen^{22–24} and Li/NH₃²⁵ reductions.

EXPERIMENTAL

Compounds I, VII, X, XIII and XIV B.D.H. reagent grade were redistilled before use. Compound III "Fluka" puriss was recrystallised from MeOH/water. Compounds VI,²⁶ IX²⁷ and XII²⁸ were prepared by acylation with Ac₂O and BF₃ from cyclohexanone, cyclopentanone and 3-methylbutane-2-one, respectively and purified by distillation. Compounds II,²⁹ V²⁶ and VIII²⁷ were obtained by methylation of III, VI and IX, respectively. Compound IV³⁰ was synthesised by LAH reduction of 5,5-dimethyl-3-methoxy-2-cyclohexene-1-one³⁰ and XI³¹ was prepared by acid rearrangement of 2,3-dimethylbutane-2,3-diol. The purity of the compounds was checked by means of VPC and TLC before each measurement.

Mercury "Merk" (G.R. and for polarography) was filtered and redistilled before use. 2-propanol was purified by distillation over NaBH₄ under N₂.⁴ Triple distilled water was used and the N₂ bubbled through the cell was purified from traces of organic and reducible substances. Tetraethylammonium-*p*-toluenesulfonate³² Et₄N-PTS was prepared from ethyl-*p*-toluenesulfonate and triethylamine, recrystallised from EtOH/ether mixtures and dried under vacuum over P₂O₅.

A dropping mercury electrode from a fine polarographic capillary served as the working electrode. The drops were knocked off every 0.20 sec by means of an electromechanical 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 min and assuming a hemispherical shape. A commercial saturated calomel electrode ("Radiometer" type K401) was used as reference and a Pt foil served as the counter electrode. All potentials reported are vs this reference electrode.

All current/potential measurements were carried out potentiostatically in 0.5 M Et₄N-PTS in isopropanol/water (4:1) using an "Elron" model CHP-1 potentiostat. The potential was varied linearly with time, at a rate of 3 mV/sec. ("Elron" model CHF-1 function generator). Current/potential curves were plotted on a 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.

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REFERENCES

- ¹ F. D. Popp and H. P. Schultz, *Chem. Rev.* **62**, 19 (1962)
- ² P. Zuman, *Coll. Czechoslov. Chem. Comm.* **33**, 2548 (1968)
- ³ P. Zuman, D. Barnes and A. Rylvova-Kejharova, *Disc. Faraday Soc.* **45**, 202 (1968)
- ⁴ B. E. Conway, E. J. Rudd and L. G. M. Gordon, *Ibid.* **45**, 87 (1968)
- ⁵ M. M. Baizer and J. D. Anderson, *J. Org. Chem.* **30**, 3138 (1965)
- ⁶ J. Weimann, *Bull. Soc. Chim. Fr* 2545 (1964)
- ⁷ S. Wawzonek and A. Gundersen, *J. Electrochem. Soc.* **111**, 324 (1964)
- ⁸ K. W. Bowers, R. W. Giese, M. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger and D. K. Roe, *J. Am. Chem. Soc.* **92**, 2783 (1970)
- ⁹ H. Adkins, F. W. Cox, *Ibid.* **60**, 1152 (1938)
- ¹⁰ R. Pasternak, *Helv. Chim. Acta* **31**, 753 (1948)
- ¹¹ D. M. Coulson and W. R. Crowell, *J. Am. Chem. Soc.* **74**, 1290 (1952); *Ibid.* 1294 (1952)
- ¹² M. Fields and E. R. Blout, *Ibid.* **70**, 930 (1948)
- ¹³ R. H. Philp, Jr., R. L. Flurry and R. A. Day, Jr., *J. Electrochem. Soc.* **111**, 328 (1964)
- ¹⁴ D. H. Evans and E. C. Woodbury, *J. Org. Chem.* **32**, 2158 (1967)
- ¹⁵ J. C. Pariaud, J. Modiano, R. Sorel and R. Stefani, *C.R. Acad. Sci., Paris* **239**, 1217 (1954)
- ¹⁶ G. Semerano and A. Chisini, *Gazz. Chim. Ital.* **66**, 504 (1936)
- ¹⁷ A. Winkel and G. Proske, *Ber. Dtsch. Chem. Ges.* **69**, 1917 (1936)
- ¹⁸ T. J. Curphey, C. W. Amelotti, T. P. Layloff, R. L. McCartney and J. H. Williams, *J. Am. Chem. Soc.* **91**, 2817 (1969)
- ¹⁹ E. Kariv, J. Hermolin and E. Gileadi, *J. Electrochem. Soc.* **117**, 342 (1970); ⁹ *Electrochim. Acta* in press.
- ²⁰ B. Eistart and W. Reiss *Ber. Dtsch. Chem. Ges.* **87**, 92, 108 (1954)
- ²¹ S. J. Cristol and R. P. Arganbright, *J. Am. Chem. Soc.* **79**, 6039 (1957); S. J. Cristoll, G. D. Brindell and J. A. Reeder, *Ibid.* **80**, 635 (1958)
- ²² E. Wenkert and E. Kariv, *Chem. Commun.* 570 (1965)
- ²³ K. M. Baker and B. R. Davis, *Chem. & Ind.* 768 (1968)
- ²⁴ N. J. Cusack and B. R. Davis, *J. Org. Chem.* **30**, 2062 (1965)
- ²⁵ W. Reusch and D. B. Priddy, *J. Am. Chem. Soc.* **91**, 3677 (1969)
- ²⁶ J. B. Payne, *J. Org. Chem.* 4796 (1961)
- ²⁷ R. M. Manyik, F. C. Frostick, Jr., J. J. Sanderson and C. R. Hauser, *J. Am. Chem. Soc.* **75**, 5030 (1953)
- ²⁸ C. R. Hauser and J. T. Adams, *Ibid.* **66**, 345 (1944)
- ²⁹ H. Thomas, *J. Chem. Soc.* 2438 (1956)
- ³⁰ R. L. Frank and H. K. Hall, *J. Am. Chem. Soc.* **72**, 1645 (1950)
- ³¹ R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry*, p. 341. (Wiley, New York) (1961)
- ³² M. M. Baizer, *J. Electrochem. Soc.* **111**, 215 (1964)