17. Reduction of 2-Bromo-4,4-dimethyl-2-cyclohexenone at Mercury. A Study on Inverted Peaks in Cyclic Voltammetry[1])

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Summary

The parameters which influence the inverted wave appearing in the reverse (oxidation) sweep in the cyclic voltammogramme of the title compound **1** are discussed in detail. The inverted wave is due to the interaction of the reduction products of **1** with the electrode and the electrolyte (TBAFB). The key condition for the presence of the inverted peak is a slow scan rate on the reverse sweep, at least for the last 50 mV before the inversion of the current-potential curve.

We recently presented [1] preliminary results on an inverted wave in the reverse (oxidation) sweep, observed in the cyclic voltammogrammes of some 2-halogeno-2-cyclohexenones[2]) [2]. Shortly after *Peters et al.* [4] reported a similar observation in the reduction of 1-iododecane at mercury. He and other authors before [5] [6] associated such an inverted wave in a cyclic voltammogramme with anomalous current maxima in the corresponding polarogrammes and they related this phenomenon to the reduction of adsorbed alkylmercury radicals. Such inverted peaks have also been observed in the reduction of phosphonium salts at mercury [7] [8]; the formation and adsorption of an amalgam was also assumed. As the number of such observations is steadily growing [9-11], indicating that the appearance of such inverted peaks could be integrated into a new analytical technique, and since reduction products of compounds such as **1**, *e.g.* α-ketovinyl anions, are useful intermediates in synthesis [12] [13], we now describe additional experimental aspects on the cyclic voltammogrammes for the reduction of the title compound in acetonitrile using tetrabutylammoniumfluoroborate as electrolyte.

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[1]) Reported at the 4th EUCHEM Conference on Organic Electrochemistry at Rodez (France), May 1980.

[2]) We observed similar phenomena with 3-chloro-2-cyclohexenones. The electrochemical reduction of such compounds has been investigated [3], but the authors do not comment on the appearance of such inverted peaks.

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We have shown [1] that the optimal conditions for observing the reduction peak in the oxidation sweep for the system **1**, Hg and TBAFB were either slow scanning or a holding period when reversing the potential. This led to cyclic voltammogrammes as shown in *Figure 1*.

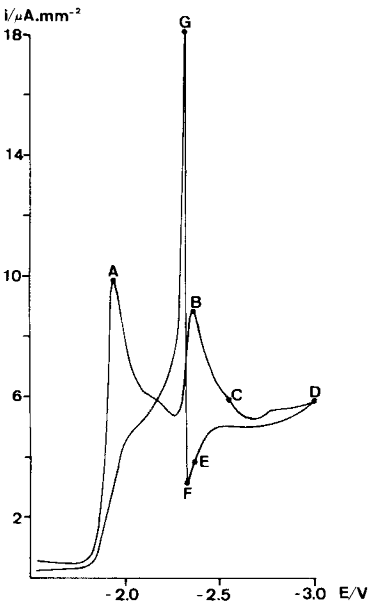


Fig. 1. *Cyclic voltammogramme of* **1** *(5.10^{-3}M in CH_3CN), TBAFB 0.5*M. Scan speed = 20 mV · s^{-1}.

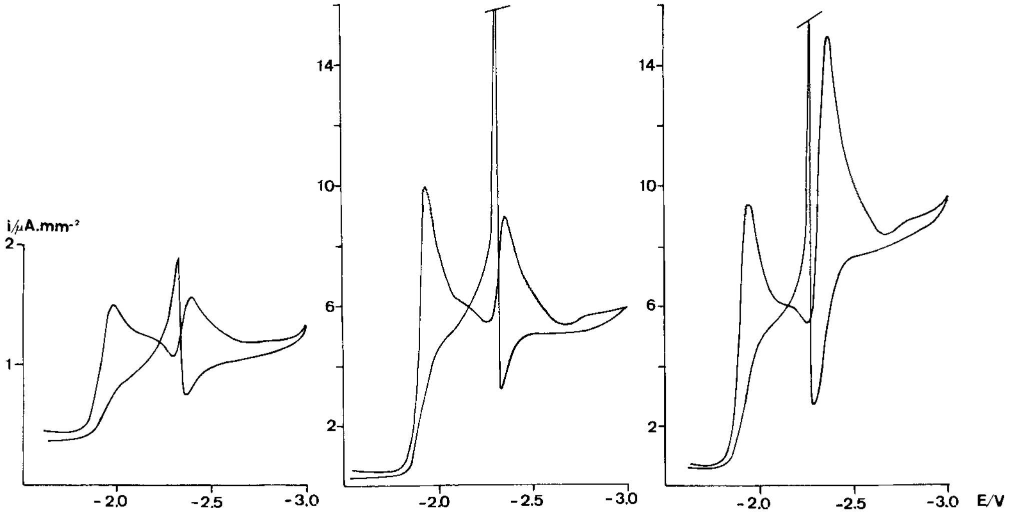


Fig. 2. *Cyclic voltammogrammes of* **1** *in CH_3CN, TBAFB 0.5*M. Scan speed = 20 mV · s^{-1}. a) 5.10^{-4}M, b) 5.10^{-3}M, c) 5.10^{-3}M + 5.10^{-3}M of 4,4-dimethyl-2-cyclohexenone.

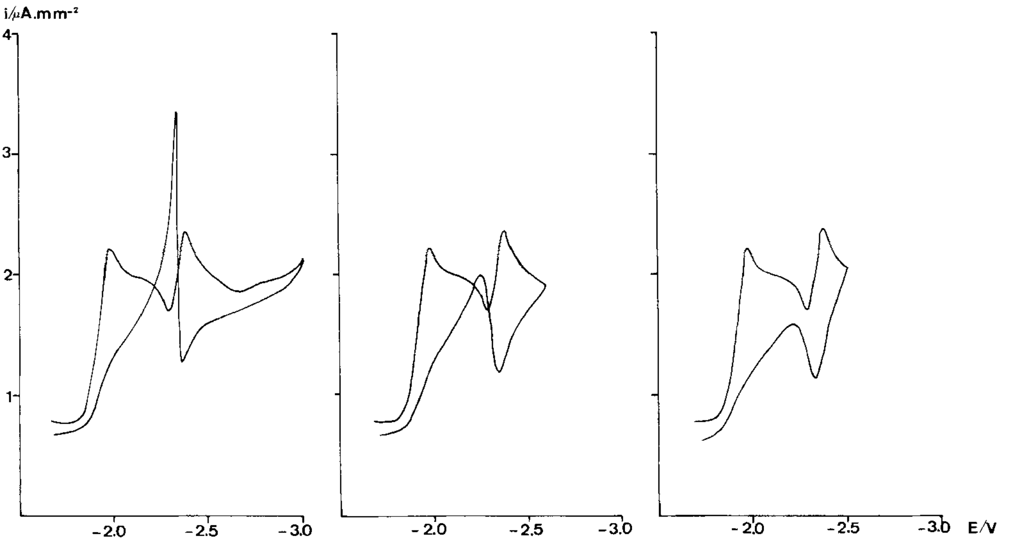


Fig. 3. *Cyclic voltammogrammes of* **1** *(10^{-3}M in CH$_3$CN), TBAFB 0.5*M. Scan speed = 20 mV · s^{-1}. Reversion potential: a) −3.0 V, b) −2.6 V, c) −2.5 V.

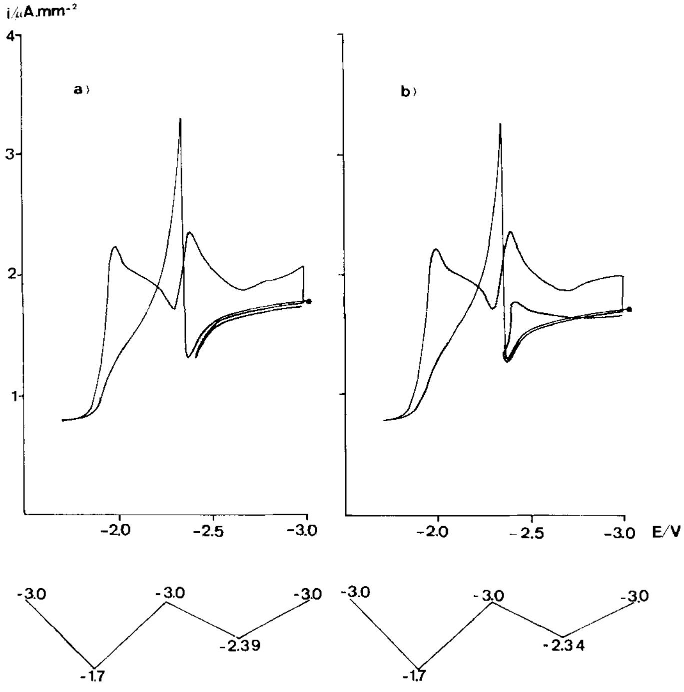


Fig. 4. *Cyclic voltammogrammes of* **1** *(10^{-3}M in CH$_3$CN), TBAFB 0.5*M. Scan speed = 20 mV · s^{-1}. Potential sequence as indicated.

For the reduction waves A and B the corresponding peak currents i_{p_A} and i_{p_B} are a function of the square root of the scan rate indicating that both steps are diffusion controlled. The ratio of i_{p_A}/i_{p_B} increases from 2.0 to 2.5 with increasing concentration of **1** (10^{-4}M to 5.10^{-3}M) for scan speeds between 20 and 2000 mV · s^{-1}. In fact i_{p_B} decreases relative to i_{p_A} with increasing concentration of **1**. The shape of the inverted peak G at a given scan rate is affected neither by the variation in concentration of **1**, nor by adding increasing amounts of 4,4-dimethyl-2-cyclohexenone (10^{-4}M-10^{-2}M) to 5.10^{-3}M **1** *(Fig. 2).*

The point C in *Figure 1* corresponds to the least cathodic reversion potential which has to be attained for the appearance of the inverted peak G. It has been determined as −2.55 V *(Fig. 3). Figure 4* shows the cyclic voltammogrammes of **1** when starting at the cathodic reversion potential D (−3.0 V), and completing a first oxidation-reduction cycle (D-H-D). The second cycle terminates at either E *(Fig. 4a)* or F *(Fig. 4b)*, and only in the latter case does the second reduction wave B reappear.

Finally a series of experiments were undertaken regarding the holding period at the reversion potential and the scan rate between the points C-D-E-F. Increasing

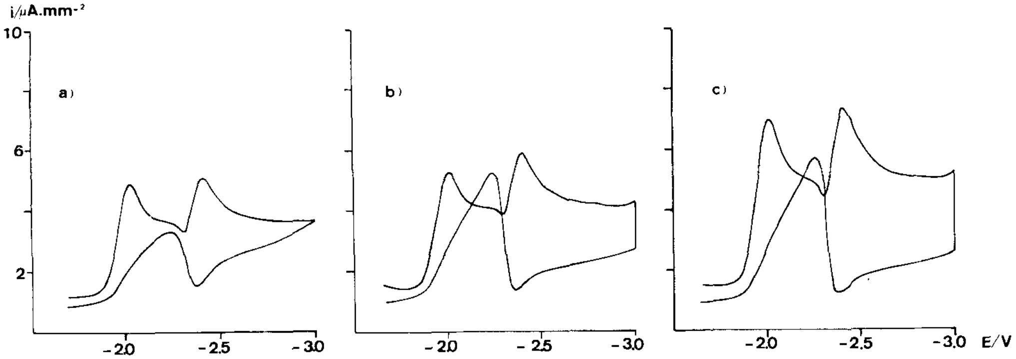


Fig. 5. *Cyclic voltammogrammes of* **1** *(10^{-3}M in CH_3CN), TBAFB 0.5*M. Scan speed = 200 mV · s^{-1}. Holding period at reversion potential D: a) 0 s, b) 20 s, c) 58 s.

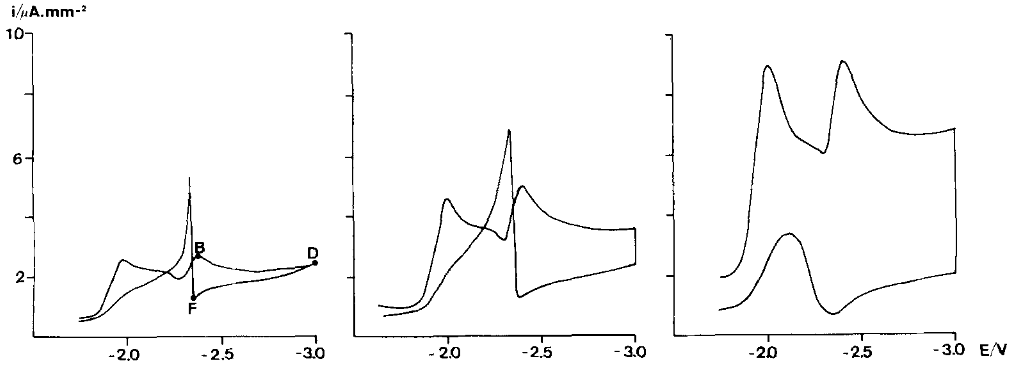


Fig. 6. *Cyclic voltammogrammes of* **1** *(10^{-3}M in CH_3CN), TBAFB 0.5*M. Constant time interval B → D → F = 64 s. Scan speed and holding period at reversion potential D: a) 20 mV · s^{-1} and 0 s, b) 100 mV · s^{-1} and 51 s, c) 500 mV · s^{-1} and 61 s.

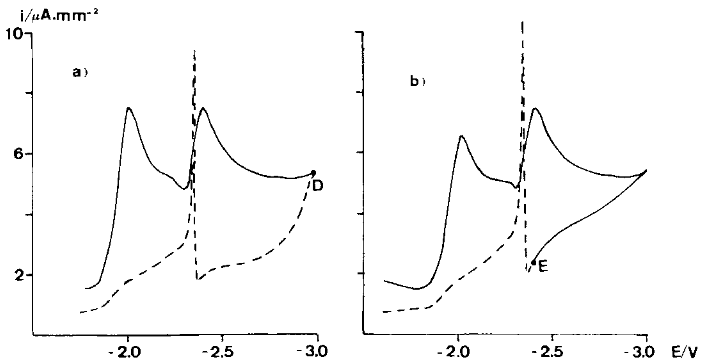
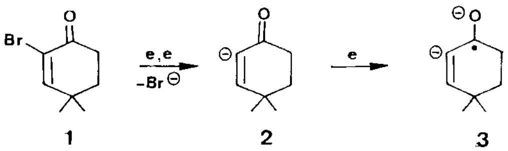


Fig. 7. *Cyclic voltammogrammes of* **1** *(10^{-3}M in CH_3CN), TBAFB 0.5*M. Scan speed: —— 200 mV · s^{-1}, ---- 20 mV · s^{-1}.

the holding period at constant scan rate hardly affects the shape of the inverted wave G *(Fig. 5). Figure 6* shows the results of keeping the time between D and F constant by varying the holding period *and* the scan rate from D to F; as can be seen, the scan rate after point F has a strong influence on the shape of G. The shape of G is similar if the scan speed (200 mV · s^{-1}) is lowered to 20 mV · s^{-1} at either D or E *(Fig. 7)*. This indicates that the key condition for the appearance of the inverted peak is a slow scan rate starting from E, *i.e.* about 50 mV before the onset of the peak.

The chemical events in the reduction of **1**, corresponding to the waves A and B, are given in *Scheme 1*.

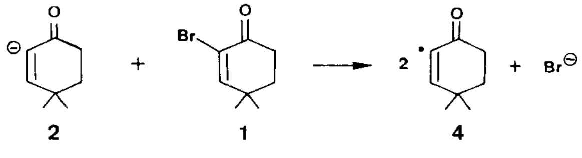
Scheme 1



From the decrease of i_{p_B} relative to i_{p_A} with increasing concentration of **1** (*Fig. 2a* and *2b*), it can be shown that **2** interacts in part with **1**. A simple proton transfer from **1** to **2** can nevertheless be excluded, as a big excess of 4,4-dimethyl-2-cyclohexenone, which should be as good a proton donor as **1** itself, does not affect the subsequent reactions *(Fig. 2c)*. This interaction between **1** and **2** can therefore be assumed to be a charge transfer giving two radicals **4** and Br^- *(Scheme 2)*.

The radical **4** could be again reduced to the carbanion **2**, or interact with mercury to give a vinylmercury radical. In related reactions where such inverted

Scheme 2



waves had been observed in the cyclic voltammogrammes [4] [6], they were attributed to either adsorption or reduction of the alkylmercury radicals formed. As we had shown [1], the presence of tetraalkylammonium cations seems to be necessary for the appearance of such inverted waves, and one has to pass beyond the second reduction wave by at least 150 mV (point C in *Fig. 1*) to observe it (*Fig. 3*). Therefore it is unreasonable to attribute the inverted wave to the presence of these organomercury radicals only.

We propose that the two-step three-electron reduction product of **1**, *i.e.* **3**, reduces the electrolyte to give **2** and tetraalkylammonium radicals which react further with mercury to give an amalgam [14]. This amalgam hinders the reduction of **1** or **2** until its reoxidation (−2.4 V), leading to the spontaneous reduction of the organic molecules. No reduction of **2** to **3** takes place without the reoxidation step (*Fig. 4*). Finally from *Figures 5–7* it is evident that this reoxidation step itself is the rate determining event for the appearance of the inverted wave, and not the electron transfer from **3** to the ammonium cation and amalgam formation, the key condition for the presence of the inverted peak G being a slow scan rate on the last 50 mV before the onset of the peak (between points E and F in *Fig. 1*).

While there is still no unambiguous explanation for the appearance of inverted peaks in cyclic voltammogrammes, investigations on the reduction of various compounds at mercury may lead to one. Subsequently, observation of these inverted peaks could lead to a new analytical technique describing the interaction of electron-transfer products with the electrode.

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Experimental Part

For cyclic voltammetry the equipment described in [1] was used. The surface of the electrode and the purification of solvent and electrolyte are also indicated in [1]. Compound **1** was synthesized following [15]. All potentials are given *vs.* Ag/10^{-2}M Ag^+.

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