Decay of Electrogenerated Dianions of Acidic Indenes: an 'Indirect' Self-protonation Mechanism

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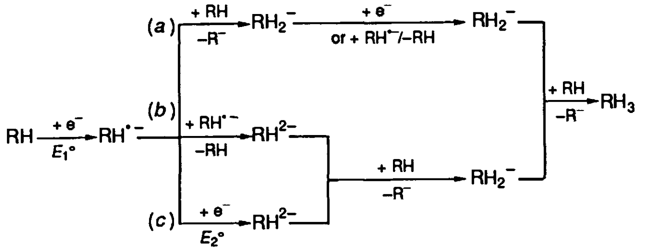
The electrode reduction of 1,2,3-triphenylindene, giving rise to the corresponding radical anion and dianion in two successive one-electron steps, was investigated in dimethylformamide with the aim of clarifying the role of the acidic substrate in the decay of the electrogenerated bases. At −50 °C the direct protonation of the radical anion by indene (self-protonation) was too slow to be effective, and the proton transfer from indene to the dianion did appear kinetically unfavourable with respect to solution electron transfer between the same species (comproportionation). However, dianion protonation by an excess of water present in the solution can induce, through the action of OH^- ions, the substrate to transform into its conjugate base. The effect resembles that predicted for a self-protonation mechanism and can be termed an 'indirect' self-protonation process. The proposed reaction scheme was confirmed by comparison of cyclic voltammetric responses with those derived by mathematical computation. The rate-constant values for the relevant steps, obtained by the fitting of experimental and computed data, are consistent with the corresponding values determined for similar compounds.

The basic reduction intermediates of organic compounds, such as anion radicals, dianions and carbanions, may undergo proton transfer from the parent compound, whenever the latter is the strongest acid present in the reaction medium.[1] This self-protonation process may occur by electrochemical reduction in dipolar aprotic solvents, not only of molecules bearing strongly acidic moieties, but also of rather weak proton donors such as C–H acids. This is the case, for instance, in the reduction of indenes bearing at least one acidic hydrogen at C-1.[2] The overall process usually involves a two-electron, two-proton reduction of one-third of the parent compound, the remaining two-thirds acting as a proton donor, being thus transformed into its conjugate base, generally reducible at much more negative potentials [see equation (1)].

$$3RH + 2e^- \longrightarrow RH_3 + 2R^- \qquad (1)$$

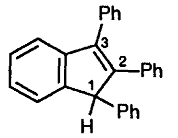
The most common reaction mechanism matching the above stoichiometry starts with the proton transfer to the primary anion radical (Scheme 1, path *a*). However, two alternative reaction mechanisms compatible with the same overall process and involving the more basic dianion should, in principle, be taken into account. The dianion may be formed either by homogeneous disproportionation of the radical anion (Scheme 1, path *b*) or by electrode reduction of the latter (Scheme 1, path *c*). It should be noted that in both cases the partners of the first proton transfer, *i.e.* the dianion and the parent compound, are involved in a competitive electron transfer, resulting in their comproportionation to anion radicals. Furthermore, should the third of the above self-protonation mechanisms be the main reaction path, a current decrease of about 30%, with respect to the one-electron level of the first reduction step, would be expected at the negative potentials where the reduction to dianion takes place. This follows from the two-electron, two-proton reduction of one-third of the parent compound taking place only at these cathodic potentials.

A current dip of this type was reported, for instance, in the reduction of diethyl fumarate in dimethylformamide (DMF) and was tentatively attributed to the proton transfer from the parent compound to the dianion, followed by coupling of the conjugate base of the former with the unreduced molecule.[3]



Scheme 1

More recently we have reported some preliminary results on the reduction, at low temperature in DMF, of 1,2,3-triphenylindene bearing an acidic hydrogen at C-1, which shows a peculiar current decrease at negative potentials, both in the polarographic and in the voltammetric pattern.[4] The effect is observed, however, only in DMF containing water, while two reversible one-electron processes occur in the ultra-anhydrous solvent. On the basis of such preliminary results we have attributed the current dip to the deprotonation of the substrate by the OH^- ions formed in the protonation of the dianion by water. The two-electron, two-proton reduction of one-third of the substrate would therefore be the consequence of what could be called an 'indirect' self-protonation.



1, 2, 3-Triphenylindene

The purpose of this paper is to get a deeper insight into the problem by comparing the experimental voltammetric results with the theoretical ones computed for the proposed mechanism, with the aim of investigating the kinetic and thermodynamic characteristics of the process and determining the pertinent rate constants.

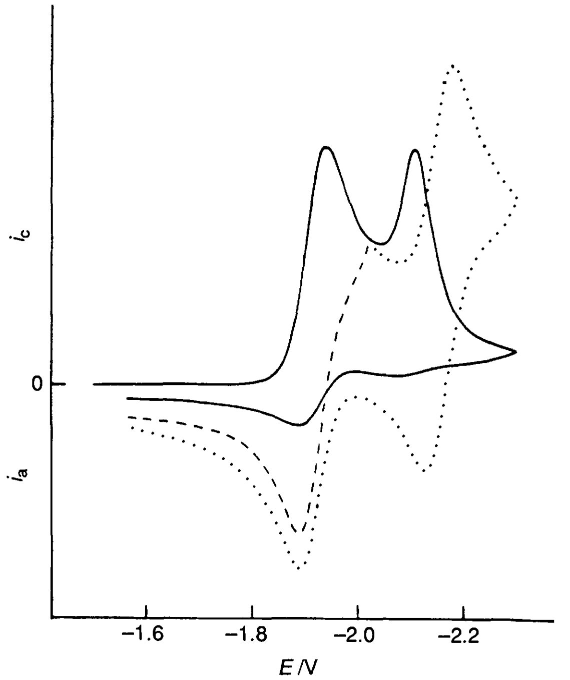


Fig. 1 Cyclic voltammograms of the indene **1** (1.0×10^{-3} mol dm^{-3}) in DMF (0.1 mol dm^{-3} TEAP) at −50 °C. Voltammetric sweep rate 0.1 V s^{-1}. (· · · ·) Under highly anhydrous conditions; (—— and – – – –) in the presence of water (0.1 mol dm^{-3}).

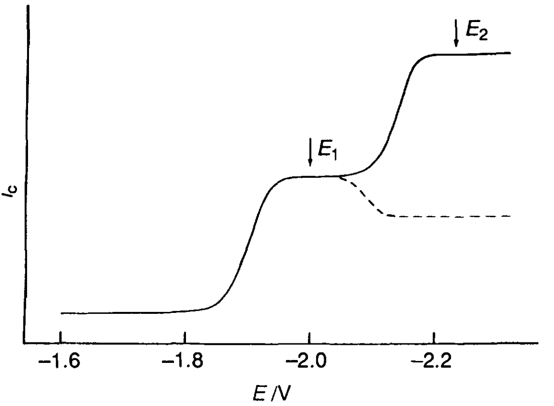


Fig. 2 Polarograms of the indene **1** (experimental conditions as in Fig. 1). Polarographic renewal time 2 s. (——) Under extremely anhydrous conditions; (– – – –) in the presence of added water. E_1 and E_2 are the potentials of the chronoamperometric curves of Fig. 3.

Results and Discussion

The electrochemical reduction of 1,2,3-triphenylindene **1** (IndH) in carefully dried DMF–0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) solution at −50 °C takes place in two chemically reversible one-electron steps (Fig. 1), even at low sweep rates (50 mV s^{-1}), corresponding to the formation of the radical anion and the dianion, respectively

$$\mathrm{IndH} + e^- \overset{E_1^\circ, k^\circ}{\rightleftharpoons} \mathrm{IndH}^{-} \qquad (2)$$

$$\mathrm{IndH}^{\cdot -} + e^- \overset{E_2^\circ}{\rightleftharpoons} \mathrm{IndH}^{2-} \qquad (3)$$

[equations (2) and (3)]. The second electron transfer is very fast, as shown by the anodic (E_p^a) to cathodic (E_p^c) peak potential difference of 44 mV in all the explored range of sweep rates (0.05–100 V s^{-1}). The first reduction step, in contrast, shows an increase of the peak potential difference at higher sweep rates (*e.g.*, 44 mV at 50 mV s^{-1}, 50 mV at 10 V s^{-1}), characteristic of a somewhat slower process.[5] The kinetic parameters for this transfer were obtained by a non-linear least-squares fitting of the experimental voltammetric curves at different sweep rates with those theoretically predicted for a quasi-reversible (Butler–Volmer kinetics) charge transfer under spherical diffusion conditions.* Owing to the small difference from completely reversible behaviour, the fitting was rather insensitive to the actual value of the transfer coefficient, which was then fixed at 0.5 in the theoretical equations. The values of the electron-transfer rate constant and of the diffusion coefficient so obtained are k° 0.3 cm s^{-1} and D 6×10^{-6} cm^2 s^{-1}, respectively.

Under the same anhydrous conditions, the polarographic pattern shows two one-electron waves of practically the same height (Fig. 2), as in the case of non-self-protonating indenes. Correspondingly, the quotient i_2/i_1 between the chronoamperometric currents detected in correspondence of the plateau of the second (i_2) and the first (i_1) reduction waves is 2.0 up to ~2 s (Fig. 3). The chemical reversibility of both steps indicates that no appreciable decay of either the radical anions or the dianions occurs *via* self-protonation reactions [equations (4) and (5), respectively].

$$\mathrm{IndH}^{\cdot -} + \mathrm{IndH} \xrightarrow{k_4} \mathrm{IndH}_2^{\cdot} + \mathrm{Ind}^- \qquad (4)$$

$$\mathrm{IndH}^{2-} + \mathrm{IndH} \xrightarrow{k_5} \mathrm{IndH}_2^{-} + \mathrm{Ind}^- \qquad (5)$$

In fact, a radical anion self-protonation [reaction (4)], which is the normal reduction path for substrate reduction at higher temperatures, could have been excluded *a priori* since the value of the corresponding rate constant, k_4, obtained by extrapolating the data at higher temperatures to −50 °C, results in too low a value to give rise to any appreciable effect even at the lowest sweep rates (at −50 °C the value is close to 1 dm^3 mol^{-1} s^{-1}, according to its activation energy).[2b] On the other hand, the lack of any proton transfer from indene to the dianion, even if this process is predicted to be rather fast, can be ascribed to an unfavourable competition with the comproportionation step [Scheme 2, reaction (6)] involving the same reagents.[4,†]

As previously reported,[4] addition of water strongly affects the electrochemical behaviour. The effect is dramatically evident in the polarographic curves at the potentials for dianion formation (Fig. 2) where, instead of the second wave, a decrease (~30%) of the one-electron limiting current is observed. Correspondingly, a chronoamperometric i_2/i_1 quotient close to 0.7 is observed for $t > 1$ s, which increases up to the value found in anhydrous conditions (i_2/i_1 2.0) for $t < 0.01$ s (Fig. 3). This behaviour implies that, in a relatively long time-scale, consumption of the substrate takes place at the second-step potentials, with the same stoichiometry as expected if the dianion self-protonation reaction were to be operating, *i.e.* with a two-electron reduction of only one-third of the starting material (Scheme 1, path *c*). However, the self-protonation scheme is excluded on the basis of the above reported results in anhydrous conditions. The mechanism represented in Scheme 2 can account for both the overall stoichiometry and the role of water in producing the effect.

In Scheme 2, the protonation reactions by water of IndH^{2-}

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* Theoretical voltammetric curves for a quasi-reversible electron transfer under semi-infinite spherical diffusion conditions can be obtained by numerically solving an integral equation similar to that pertaining to linear diffusion.[6a–c] Just a different kernel in the equation accounts for the spherical electrode geometry.[6d]

† These factors were considered by Kiesele and Evans for similar compounds.[7]

$$\mathrm{IndH} + e^- \xrightleftharpoons{E^\circ_1, k^\circ} \mathrm{IndH}^{\bullet -} \qquad (2)$$

$$\mathrm{IndH}^{\bullet -} + e^- \xrightleftharpoons{E^\circ_2} \mathrm{IndH}^{2-} \qquad (3)$$

$$\mathrm{IndH}^{2-} + \mathrm{IndH} \xrightleftharpoons[k_{-6}]{k_6} 2\mathrm{IndH}^{\bullet -} \qquad (6)$$

$$\mathrm{IndH}^{2-} + \mathrm{H_2O} \xrightarrow{k_7} \mathrm{IndH_2^-} + \mathrm{OH^-} \qquad (7)$$

$$\mathrm{IndH_2^-} + \mathrm{H_2O} \xrightarrow{k_8} \mathrm{IndH_3} + \mathrm{OH^-} \qquad (8)$$

$$\mathrm{IndH} + \mathrm{OH^-} \xrightarrow{k_9} \mathrm{Ind^-} + \mathrm{H_2O} \qquad (9)$$

Scheme 2

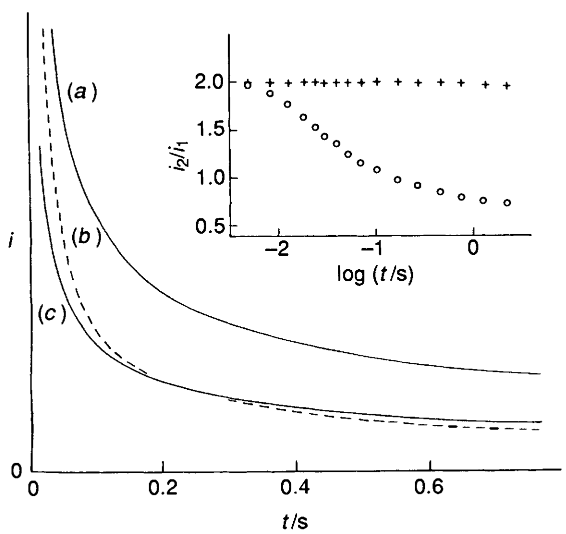

Fig. 3 Chronoamperometric curves for the indene **1** at the potentials E_1 and E_2 reported in Fig. 2 (experimental conditions as in Fig. 1). (a) At E_2, under highly anhydrous conditions; (*b*) at E_2, in the presence of added water; (*c*) at E_1, under both conditions. Inset: plot of the quotient i_2/i_1 between the currents detected at E_2 and E_1, *vs.* log *t*. (+) Under highly anhydrous conditions; (○) in the presence of added water.

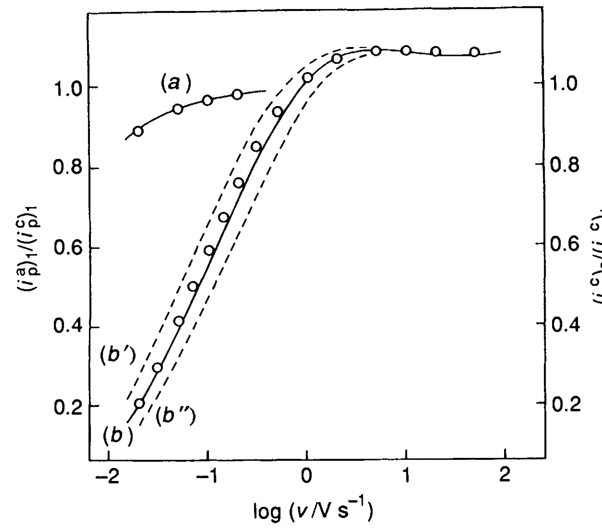

Fig. 4 Voltammetric peak current ratios (*a*) $(i^a_p)_1/(i^c_p)_1$ and (*b*) $(i^c_p)_2/(i^c_p)_1$ as functions of v for the indene **1** in the presence of water (experimental conditions as in Fig. 1). (○) Experimental data. Solid and dashed lines represent the data calculated for the following rate-constant values: k_6: 5 × 10^7 dm^3 mol^{-1} s^{-1}; k_7: 8 × 10^3 dm^3 mol^{-1} s^{-1}; k_9: (*a*) and (*b*) 3 × 10^4, (*b′*) 1.5 × 10^4, (*b″*) 4.5 × 10^4 dm^3 mol^{-1} s^{-1}.

[equation (7)] and $\mathrm{IndH_2^-}$ [equation (8)] were considered as irreversible on the basis of the low acidity of $\mathrm{IndH_3}$ (and hence of $\mathrm{IndH_2^-}$) with respect to water. As a matter of fact, addition of tetrabutylammonium hydroxide to a solution of 1,2,3-triphenylindane ($\mathrm{IndH_3}$) in DMF does not generate any appreciable oxidation peak for the anions $\mathrm{IndH_2^-}$ * and $\mathrm{IndH^{2-}}$, indicating that backward reactions (7) and (8) can be neglected. Furthermore, addition of water to a solution containing $\mathrm{Ind^-}$ † does not cause the reduction peaks of IndH to be formed, indicating that the deprotonation of the indene [reaction (9)] is practically irreversible. This is in line with the pK_a values of IndH and water in Me$_2$SO (15.2[8a] and 31.4,[8b] respectively).

The reaction sequence (Scheme 2) was used to compute the theoretical behaviour for the voltammetric reduction at different sweep rates (see Appendix for details) with a 100:1 excess of water over substrate. The influence of the kinetic processes in the voltammetric curves is more subtle than that observed in the polarographic experiments, yet the sweep-rate dependence of the characteristic quantities of the curves (peak potentials, anodic and cathodic peak currents) allows all the relevant rate constants to be determined. In the theoretical approach the assumption was made of a steady-state condition for $\mathrm{IndH_2^-}$, which corresponds to neglect of the kinetic contribution of reaction (8) and simply to consider the rate of disappearance of water as being twice that of $\mathrm{IndH^{2-}}$. Such an assumption is justified by the non-detection of the $\mathrm{IndH_2^-}$ oxidation peak in DMF solutions of IndH containing water (0.1 mol dm^{-3}), even at high sweep rates (100 V s^{-1}), implying that its concentration must be very low in the reaction layer.

In Scheme 2, the fast solution electron transfer (SET)[9] between the dianion and the neutral molecule [comproportionation, equation (6)], and the backward radical anion disproportionation were properly taken into account. The existence of the latter can explain the small decay observed for the radical anion at slow sweep rates, as shown by the slight decrease of the quotient, $(i^a_p)_1/(i^c_p)_1$, of the anodic to cathodic peak current for the first step [Fig. 4, curve (*a*)]. The disproportionation reaction is thermodynamically unfavourable, having $K_6 = k_{-6}/k_6 = 6.0 \times 10^{-6}$ (as obtained by the standard potential difference measured in anhydrous conditions, $E^\circ_1 - E^\circ_2 = 0.231$ V), but is driven by the following dianion protonation by water [equation (7)]. The corresponding rate constants, obtained by comparison of the experimental and computed data, are k_6 5 × 10^7 dm^3 mol^{-1} s^{-1} and k_{-6} 3 × 10^2 dm^3 mol^{-1} s^{-1}. The value for the comproportionation reaction k_6 can be compared with those obtained, at temperatures higher than −50 °C, with other 2,3-diphenyl-substituted indenes for which a radical anion decay

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* In the presence of low concentration of water (*e.g.*, 10^{-2} mol dm^{-3}) and at high sweep rates (50 V s^{-1}), by reversing the potential sweep after a cathodic scan up to the second reduction step, it is possible to detect the reversible oxidation peak of the anion $\mathrm{IndH_2^-}$ formed by protonation of the dianion by water, as observed in the case of non-self-protonating indenes[2a] [equation (10)]. The oxidation peak is absent

$$\mathrm{IndH_2^-} \rightleftharpoons \mathrm{IndH_2^{\bullet}} + e^- \qquad (10)$$

both in carefully anhydrous solutions, owing to the non-protonation of $\mathrm{IndH^{2-}}$, and in the presence of large amounts of water because of the fast protonation of $\mathrm{IndH_2^-}$.

† The anion $\mathrm{Ind^-}$ was produced by exhaustive electrolysis of IndH at 25 °C, *i.e.* under conditions where the self-protonation reduction mechanism (Scheme 1, path *a*) is operating.

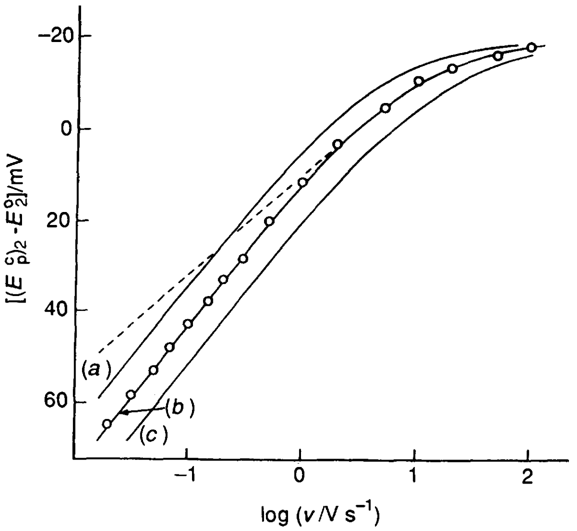

Fig. 5 Voltammetric peak potential for the second step of reduction of the indene **1** as a function of *v* in the presence of water (experimental conditions as in Fig. 1). (○) Experimental data. Solid lines are the data calculated for the following rate-constant values: k_6: 5 × 10^7 dm^3 mol^{-1} s^{-1}; k_9: 3 × 10^4 dm^3 mol^{-1} s^{-1}; k_7: (a) 4 × 10^3, (b) 8 × 10^3, (c) 16 × 10^3 dm^3 mol^{-1} s^{-1}. The dashed line represents the data calculated as for (b) with k_9 0.

via disproportionation and dianion protonation was observed in the presence of water.[2a] Extrapolation of these values to −50 °C gives rate constants of the order of 10^8 dm^3 mol^{-1} s^{-1}, *i.e.* slightly greater than the present one. However, the lower value found here can be easily explained[10] by the smaller driving force for the SET reaction, as shown by the smaller difference between the redox potentials with respect to that of, for instance, 1-methyl-1,2,3-triphenylindene **2** ($E^\circ_1 - E^\circ_2$ 0.335 V).

Since the disproportionation–dianion protonation is the usual path in the decay of anion radicals of other 2,3-diphenyl-substituted indenes,[2a] in the present case also the alternative direct protonation of $\mathrm{IndH^{\bullet -}}$ by water [equation (11)] should

$$\mathrm{IndH^{\bullet -}} + \mathrm{H_2O} \xrightarrow{k_{11}} \mathrm{IndH^{\bullet}_2} + \mathrm{OH^-} \qquad (11)$$

play a negligible role. This is tantamount to assuming that reaction (11) is slower than the reverse of reaction (6), *i.e.* that $k_{11}[\mathrm{IndH^{\bullet -}}][\mathrm{H_2O}] \ll k_{-6}[\mathrm{IndH^{\bullet -}}]^2$ or that $k_{11} \ll 3$ dm^3 mol^{-1} s^{-1}, tentatively $k_{11} \leqslant 0.1$ dm^3 mol^{-1} s^{-1}.

As regards the second reduction step, its height and position are little affected by the presence of water at high sweep rates, and yet the very low reversibility (as measured by the anodic component of the peak), which completely disappears for $v < 50$ V s^{-1}, shows that the dianion is unstable. The absence of an anodic component is coupled to a positive shift of the cathodic peak (Fig. 5), whereas the cathodic-peak current maintains its one-to-one value (or nearly so)* with that of the first one-electron step (Fig. 4). The behaviour is typical of a simple electron transfer followed by a homogeneous chemical reaction and indicates a quantitative protonation of the dianion by water but practically no consumption of the substrate in a non-electrochemical pathway. Only for $v < 1$ V s^{-1} is a sensible decrease of the cathodic current observed, which is stronger in the descending branch and ultimately causes the diffusion-controlled current to drop below the extension of the first step (the voltammetric counterpart of the polarographic decrease in the limiting current). Correspondingly, by lowering the sweep rate the peak potential exhibits an anodic shift (31 mV/log *v*) larger than that expected for a simple irreversible protonation of the dianion by water under kinetic control (22 mV/log *v* at −50 °C,[6c] dashed line in Fig. 5).

Such behaviour is correctly predicted by the simulation (Figs. 4, 5 and 6) as being due to the protonation of the dianion [equation (7)] and of the monoanion $\mathrm{IndH_2^-}$ [equation (8)] by water close to the electrode surface where no more indene is present at the second-step potentials. The following deprotonation of the indene by $\mathrm{OH^-}$, responsible for the decrease of the second peak current, can only occur after diffusion of this basic species towards the bulk solution where the indene concentration is appreciable. Even if the corresponding rate constants obtained by the fitting of computed and experimental data, k_7 8 × 10^3 dm^3 mol^{-1} s^{-1}, k_9 3 × 10^4 dm^3 mol^{-1} s^{-1}, should favour the indene deprotonation, the low concentrations of the two reagents (IndH, $\mathrm{OH^-}$) in the same space region makes this reaction slower than dianion decay, and explains why the two processes are not simultaneous.

The value obtained for k_7 (the rate constant for the dianion's protonation by water) can be compared with that observed in the case of the indene **2** for the same reaction under identical conditions (4 × 10^4 dm^3 mol^{-1} s^{-1}).[12] The present lower value can be attributed to a higher stability of the corresponding dianion, in agreement with the little more positive E°_1-value (~40 mV) and the much more positive E°_2-value (~140 mV) for the indene **1** with respect to compound **2**. These effects are presumably due to smaller steric hindrance of the hydrogen atom compared with that of the methyl group at C-1, which allows better delocalization of the unpaired electron of $\mathrm{IndH^{\bullet -}}$ on the phenyl group at C-2 and, in greater extent, of the negative charge of $\mathrm{IndH^{2-}}$.

On the basis of the much greater thermodynamic acidity of the indene **1** with respect to water,[8] one would expect a greater rate constant for the protonation of $\mathrm{IndH^{2-}}$ by the indene [reaction (5)]. Actually, as noted above, the absence of any effect on the voltammetric pattern in anhydrous conditions shows that such a rate constant cannot be very large, at least if compared with the SET rate constant, k_6. Voltammetric curves calculated to reproduce the behaviour in the absence of any exogenous proton donor, *i.e.* for a reaction scheme implying the steps (2), (3), (5) and (6), showed that k_5 must be at least one-hundredth of k_6 in order that any significant effect be observed. The lack of such effects, even at the lowest sweep rates, together with the previously determined value for k_6, sets an upper limit to the dianion self-protonation rate constant, *viz.* $k_5 \leqslant 5 \times 10^5$ dm^3 mol^{-1} s^{-1}.

As it can be seen, the difference in thermodynamic acidity between the two acids, the indene and water, is not paralleled by a corresponding difference in kinetic acidity. However, a comparison between them is not straightforward, due to the different bond involved in the proton-transfer step (C–H or O–H in our case) and the different electronic and steric effects exerted by the group(s) bonded at the carbon or oxygen atoms. These facts could make the kinetic acidity of the carbon acid much smaller than expected on the basis of the thermodynamic acidity constant, and hence render k_5 not much greater than k_7, as observed. The same considerations can explain the small kinetic difference between the IndH deprotonation by $\mathrm{OH^-}$ [reaction (9)] and its reaction with $\mathrm{IndH^{2-}}$ [reaction (5)] as compared with the expected large difference in thermodynamic basicity. A lower reactivity of carbon-acids with respect to that of oxygen- or nitrogen-acids is frequently reported.[13]

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* When no appreciable deprotonation of IndH takes place ($1 < v < 20$ V s^{-1}) the peak current of the second reduction peak is slightly higher than that of the first (Fig. 4). This is in agreement with the theoretical prediction for an EC-type mechanism[6c,11] which indicates an increase of the peak-current function up to ~10% with respect to the value for a simple reversible charge transfer. This behaviour has been observed, under the same experimental conditions, in the case of the indene **2**.

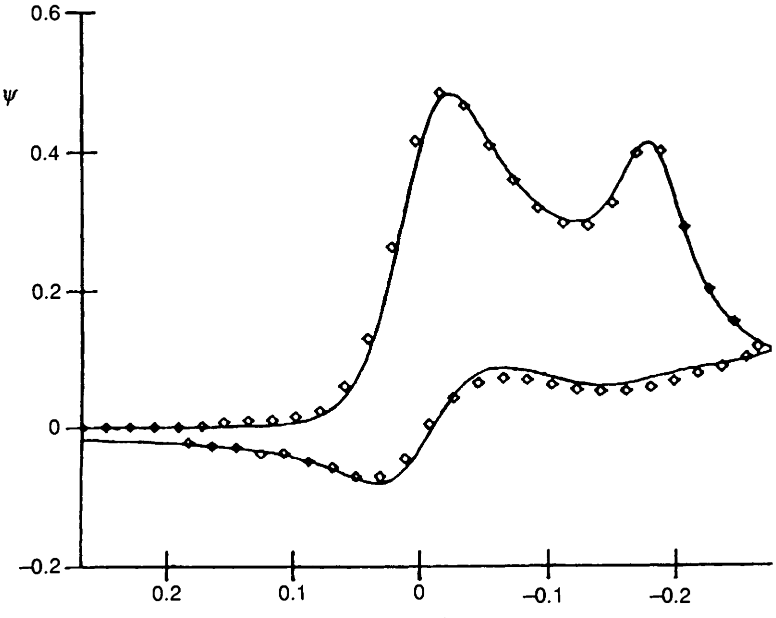

Fig. 6 Experimental (◇) and simulated (——) voltammograms at 50 mV s^{-1} for the indene **1** in the presence of water (experimental conditions as in Fig. 1). ψ Is the dimensionless current $i/[FSC_s(F v D/RT)^{\frac{1}{2}}]$ (current function). Calculated data correspond to the following rate-constant values: k_6: 5 × 10^7 dm^3 mol^{-1} s^{-1}; k_7: 8 × 10^3 dm^3 mol^{-1} s^{-1}; k_9: 3 × 10^4 dm^3 mol^{-1} s^{-1}.

Finally, one can compare the kinetic basicity of $IndH^{2-}$ and $IndH^{\bullet -}$ towards the same proton donor, either IndH or water, on the basis of estimated values for the protonation rate constants of the radical anion [reactions (4) and (11)]. The difference between the dianion and the radical anion as given by the quotient of the protonation rate constant by IndH, k_5/k_4, and that by water, k_7/k_{11}, is $<5 \times 10^5$ and $>8 \times 10^4$, presumably close to 10^5, *i.e.* in agreement with the stronger basicity of the doubly charged species.

Conclusions.—At low temperatures the acidic compound 1,2,3-triphenylindene is reduced to the corresponding radical anion and the dianion in two separate steps. In spite of its basicity, the dianion does not react with the substrate *via* a proton-transfer reaction since the two reagents are involved in a faster step, the solution electron transfer. The peculiar behaviour found at the potentials where the dianion is formed, implying a non-electrochemical consumption of the substrate, can only occur owing to the presence of water in the solution. The exogenous proton donor, even if less acidic than the substrate, is favoured to protonate the dianion because of its higher concentration at the electrode. The involvement of the parent compound in an acid–base reaction only takes place as the last step by means of the conjugate base of the exogenous proton donor, giving rise to what can be called an 'indirect' self-protonation.

The conclusions arrived at in the specific case can actually have a more general validity. When a substrate is involved in two successive, rather fast, electron-transfer steps, its comproportionation reaction with the product of the second step is thermodynamically favoured, with a rate which can easily reach the diffusion limit. Any other kind of interaction between the same species can give rise to detectable effects only if its rate is comparable with that of the former, a case not very frequent for reactions involving bond-breaking and -forming. However, if the interaction implies a proton-transfer step, it can become operational through a sequence of steps by the mediating action of proton donors accidentally present in the solution. The observed behaviour is qualitatively similar to the direct interaction and can lead to erroneous deductions being made concerning the mechanism of the reaction.

Experimental

Chemicals.—DMF (R. P. Erba) was distilled under reduced pressure and stored over activated neutral alumina under nitrogen. TEAP (R. P. Erba) was recrystallized from methanol and dried *in vacuo* at 60 °C. 1,2,3-Triphenyl-1*H*-indene **1** and 1-methyl-1,2,3-triphenyl-1*H*-indene **2** were prepared as previously described.[2a] Doubly distilled water was used as a proton donor. Neutral alumina (Merck, activity grade I) was activated by heating at 350 °C overnight *in vacuo* and then stored under dry nitrogen.

Apparatus.—Electrochemical measurements were performed with a Princeton Applied Research (PAR) model 175 universal programmer connected to a PAR model 173 potentiostat-galvanostat equipped with a PAR model 179 digital coulometer, using positive feedback to compensate for the ohmic drop. Polarographic data were directly displayed on an *X–Y* recorder, while voltammetric and amperometric measurements were previously recorded on a Nicolet model 3091 digital oscilloscope. Cell and electrodes are as previously reported.[2a] Numerical simulations of the voltammetric experiments were performed on a μVAX II computer (DEC).

Procedures.—All the experiments were carried out in DMF with TEAP (0.1 mol dm^{-3}) as supporting electrolyte, at −50 °C, with 0.1 mol dm^{-3} of water when added. As regards the voltammetric kinetics, the values of $(i_p^a)_1$ and $(i_p^c)_2$ were measured with respect to the baseline recorded by stopping the cathodic sweep at a potential 0.080 V more negative than E_1°; the values thus obtained were corrected for the capacitive and background currents.

Appendix

The reaction sequence of Scheme 2, together with the steady-state assumption for $[IndH_2^-]$ and the conditions of mass conservation for $[H_2O]$ and $[OH^-]$ ($[H_2O] + [OH^-] = C_w$, the water analytical concentration), give rise to the following system of four partial differential equations (A1–A4) with the corresponding initial and boundary conditions (A5–A10).

$$\partial A/\partial t = D[\partial^2 A/\partial r^2 + (2/r)(\partial A/\partial r)] - k_6(AC - K_6B^2) - k_9AQ \quad \text{(A1)}$$

$$\partial B/\partial t = D[\partial^2 B/\partial r^2 + (2/r)(\partial B/\partial r)] + 2k_6(AC - K_6B^2) \quad \text{(A2)}$$

$$\partial C/\partial t = D[\partial^2 C/\partial r^2 + (2/r)(\partial C/\partial r)] - k_6(AC - K_6B^2) - k_7C(C_w - Q) \quad \text{(A3)}$$

$$\partial Q/\partial t = D[\partial^2 Q/\partial r^2 + (2/r)(\partial Q/\partial r)] + 2k_7C(C_w - Q) - k_9AQ \quad \text{(A4)}$$

$$t = 0, r \geqslant r_0: A = C_s, B = C = Q = 0 \quad \text{(A5)}$$

$$t > 0, r \rightarrow \infty: A = C_s, B = C = Q = 0 \quad \text{(A6)}$$

$$t > 0, r = r_0: D(\partial A/\partial r + \partial B/\partial r + \partial C/\partial r) = 0 \quad \text{(A7)}$$

$$D(\partial Q/\partial r) = 0 \quad \text{(A8)}$$

$$D(\partial A/\partial r) = k^{\circ} \exp[-\alpha F(E - E_1^{\circ})/RT] \{A - B\exp[\mathrm{F}(\mathrm{E} - \mathrm{E}_1^{\circ})/RT]\} \quad \text{(A9)}$$

$$B = (C/K_6) \exp[F(E - E_1^{\circ})/RT] \quad \text{(A10)}$$

They represent the diffusion of the species towards a spherical electrode (radius r_0, electrode surface S), with the assumption of a common value (D) for the diffusion coefficients, and the homogeneous reactions of Scheme 2 for IndH (A), $\mathrm{IndH}^{\bullet -}$($B$), IndH^{2-}(C) and OH^- (Q). The initial and boundary conditions express the fact that, of these four species, only IndH is initially present in solution (C_s is its analytical concentration), that the diffusion is semi-infinite, that the fluxes of IndH, $\mathrm{IndH}^{\bullet -}$ and IndH^{2-} at the electrode are bound by the two charge-transfer reactions, and that OH^- is electroinactive. They also describe the characteristics of the two electron transfers, as deduced by experiments under anhydrous conditions: the first is quasi-reversible, with a rate constant depending on the applied potential (E) according to a Butler–Volmer relationship, whereas the second is Nernstian.

In the context of a cyclic voltammetry experiment, the applied potential is related to the initial potential of the scan (E_i), to the time (t), the inversion time of the sweep (t_{inv}) and the scan rate (v) according to equations (A11) and (A12).

$$E = E_i - vt \text{ for } t \leqslant t_{\text{inv}} \quad \text{(A11)}$$

$$E = E_i + v(t - 2t_{\text{inv}}) \text{ for } t > t_{\text{inv}} \quad \text{(A12)}$$

The response to be sought for is the total current, $i = i_1 + i_2$, sum of the components due to the two charge transfers, as given by equation (A13), as a function of the applied potential.

$$i_1/FS = D(\partial A/\partial r)_{r=r_0}, i_2/FS = -D(\partial C/\partial r)_{r=r_0} \quad \text{(A13)}$$

The computation was performed by expressing the equations in terms of dimensionless variables and parameters. By using for some dimensionless parameters [the one related to the electrode radius $(RTD/Fv)^{\frac{1}{2}}/r_0$, the value of the equilibrium constant K_6, the transfer coefficient α and the dimensionless standard-rate constant for the first electron transfer $k_2^{\circ}(RT/FvD)^{\frac{1}{2}}$] values obtained in the absence of protonation reactions (anhydrous conditions), and the experimental value for the quotient C_w/C_s, the solutions depend on three dimensionless parameters, RTC_sk_6/Fv, RTC_sk_7/Fv and RTC_sk_9/Fv, describing the competition between the homogeneous reactions and the diffusion. The system of differential equations was solved by means of an implicit (Crank–Nicolson) finite-difference procedure,[14] with an exponentially expanding space grid.[15]

Voltammograms were calculated for different values of the above parameters in order to obtain the variation of $(i_p^a)_1/(i_p^c)_1$, $(i_p^c)_2/(i_p^c)_1$ and $(E_p^c)_2$ with the sweep rate. The best fit between experimental and calculated data is shown in Figs. 4 and 5 for the rate-constant values reported in the text. In these figures are also shown, as a comparison, some theoretical curves obtained for slightly different values of the rate constants. In Fig. 5 we also report the computed $(E_p^c)_2$ dependence on the sweep rate for the case of irreversible protonation of the dianion by water without deprotonation of IndH. A voltammogram calculated on the basis of the above reported rate-constant values is compared with an experimental curve in Fig. 6.

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