Protonation Kinetics of Anionic Intermediates in the Electrochemical Reduction of Triphenylethylene: a Disproportionation Mechanism

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The voltammetric behaviour of triphenylethylene (T) in dimethylformamide in the presence of traces of proton donor indicates that the radical anion ($T^{-\bullet}$) is stable, the dianion (T^{2-}) is rapidly protonated, and the resulting carbanion (TH^{-}) is a relatively strong base. In the presence of added water, $T^{-\bullet}$ decays *via* disproportionation followed by protonation of T^{2-}. This was indicated by both homogeneous and voltammetric kinetics. In fact, in homogeneous conditions, the rate of decay is second-order in $[T^{-\bullet}]$, enhanced by water, and inhibited by T. Voltammetric kinetics further support the proposed mechanism showing that, under particular conditions, the reaction is rate-limited by the disproportionation step. Alternative mechanisms can be disregarded on the basis of both kinetic and thermodynamic data.

THE protonation mechanisms of radical anions of aromatic compounds have been extensively studied. On the basis of the overall stoicheiometry (1) where ArH_2 is

$$2\,Ar^{-\bullet} + 2\,HS \longrightarrow ArH_2 + Ar + 2\,S^{-} \qquad (1)$$

the dihydro-product of the aromatic substrate and HS is the proton donor, the first mechanism proposed[1] was that in Scheme 1. Scheme 1 is based on a relatively high

$$\begin{aligned} Ar^{-\bullet} + HS &\longrightarrow ArH^{\bullet} + S^{-} \\ ArH\cdot + Ar^{-\bullet} &\longrightarrow ArH^{-} + Ar \\ ArH^{-} + HS &\longrightarrow ArH_2 + S^{-} \end{aligned}$$

SCHEME 1 Regeneration mechanism

basicity of the radical anion and on the fact that the neutral radical $ArH^{\bullet}$ has a higher electron affinity than the parent substrate.[2]

Studies of the homogeneous kinetics and electrochemistry have tested the mechanism and revealed different kinetic behaviour depending on the class of substrates and/or the acidity of the proton donor; in particular, each step can be rate-determining.[3-9]

On the other hand, some papers on the protonation of perylene and anthracene radical anions by alcohols or water revealed the occurrence of another reaction pathway, *e.g. via* dianions as the bases.[4-7,10] Disproportionation of radical anions is generally an unfavourable equilibrium but, on the other hand, dianions are highly reactive bases.[11,12] Thus, Scheme 2 can compete with Scheme 1.

$$\begin{aligned} 2\,Ar^{-\bullet} &\rightleftharpoons Ar^{2-\bullet} + Ar \\ Ar^{2-} + HS &\longrightarrow ArH^{-} + S^{-} \\ ArH^{-} + HS &\longrightarrow ArH_2 + S^{-} \end{aligned}$$

SCHEME 2 Disproportionation mechanism

Overall, it can be observed that the direct protonation of the radical anions is preferred but sometimes the dianions provide an easier route to the products.

In the search for a better understanding of the mechanism of the decay of radical anions *via* protonation, we have thoroughly investigated the reduction of phenyl-activated ethylenes in dimethylformamide (DMF). Although the cyclic voltammetric behaviour of some of these compounds has been qualitatively interpreted on the basis of a disproportionation of the electrogenerated radical anions followed by protonation of the dianions,[13] the overall reduction mechanism of such a class of substrates is still a somewhat open problem as some existing information is qualitative and controversial.[13,14]

In this paper, triphenylethylene was chosen owing to the moderate stability of its radical anion towards proton donors like water.

EXPERIMENTAL

Materials and Apparatus.—Triphenylethylene (Ega Chemie) was recrystallized from a 1 : 3 benzene–methanol solution, m.p. 72—73 °C. The purification of DMF and the preparation of tetrabutylammonium perchlorate were carried out as previously described.[15] Twice-distilled water was used as the proton donor. Neutral alumina (Merck; activity grade I) was activated by heating overnight at 350 °C in vacuum, then cooled and stored under dry nitrogen.

Polarographic, amperometric, and potential-sweep voltammetric measurements were performed with an AMEL model 566 function generator, connected to a model 551 potentiostat and a model 563 multipurpose unit, using positive feedback to compensate for the ohmic drop. Polarographic and amperometric data were directly displayed on a Hewlett–Packard model 7040 A *X–Y* recorder, while voltammetric measurements were previously recorded on a Gould model OS 4 100 digital storage oscilloscope. Controlled-potential electrolysis and coulometric measurements were performed with an AMEL model 552 potentiostat equipped with a model 558 current integrator.

A three-electrode cell was employed and measurements were carried out under nitrogen. The temperature of the solution was kept constant, within 0.2 °C, by circulation of thermostatted water or ethanol through the double wall of the cell.

The working electrode was a platinum sphere, sealed into glass, electrolytically covered by a thin layer of silver and then amalgamated by dipping in mercury. The mechanical renewal of the diffusion layer, in potentiostatic measurements, has been discussed previously.[16] Electrolyses were carried out with a mercury-pool cathode. Ag–AgCl–tetramethylammonium chloride (saturated solution) in 3 : 1 acetonitrile–DMF was used as reference electrode. A Pt wire in a DMF–Bu_4NClO_4 solution was used as counter electrode. A plug of methylcellulose gel (made with the latter solution) served as the separator of both electrodes.

Procedure.—In order to investigate the voltammetric behaviour in anhydrous conditions, activated alumina was added to the cell.[17] The amount of water in the solution was varied by using different amounts of alumina.

Before each kinetic experiment the solution was cycled through a column of alumina[18] and then water was injected into the cell. Homogeneous kinetic runs were carried out by monitoring the decrease of the limiting oxidation current of the radical anion, produced by electrolysis, at a fixed potential *ca.* 300 mV more positive than the reversible potential of the T–$T^{-\bullet}$ pair. As regards the voltammetric kinetics, the values of the ratio (i_a/i_c) of anodic to cathodic peak currents were calculated by the method proposed by Nicholson and his co-workers.[19] The i_a/i_c working curve was chosen, for each kinetic measurement, taking into account the shape of the electrode and the experimental conditions.[20]

All measurements were carried out with [Bu_4NClO_4] 0.1M. Triphenylethane was obtained quantitatively after exhaustive electrolysis. The electrolysed solution was concentrated under vacuum and the residual was washed with twice-distilled water in order to eliminate the supporting electrolyte. The final product was crystallized and then identified by elemental and spectral (i.r. and ^1H n.m.r.) analyses.

RESULTS

Voltammetric Behaviour.—As previously reported by Troll and Baizer,[13] the electrochemical reduction in DMF of the olefinic bond of triphenylethylene (T) takes place in two one-electron steps (2) and (3) where $T^{-\bullet}$ is the radical anion

$$T + e^- \rightleftharpoons T^{-\bullet} \qquad (2)$$

$$T^{-\bullet} + e^- \rightleftharpoons T^{2-} \qquad (3)$$

and T^{2-} the dianion.

In a cyclic voltammetry (c.v.) experiment the first reduction step is reversible while the reduction of the radical anion is profoundly affected by the presence of traces of proton donors (in particular water) which render the corresponding peak chemically irreversible. This behaviour is in agreement with strong basicity of the dianion which is protonated to give the monoanion TH^-. The stability of the dianion is sensibly enhanced in the presence of suspended neutral alumina,[17] even at the lowest scan rates, as can be seen in Figure 1. Its peak potential, however, is affected by the scan rate when $v > 1$ V s^{-1} indicating a quasireversible heterogeneous electron transfer which can likely be attributed to the Bu_4N^+ counterions.[21]

The difference in peak potentials between the two reductions steps in completely reversible conditions allows the determination of the disproportionation equilibrium constant K_d of the radical anions. Reliable values of the second peak potential were not obtained at $T > 30$ °C.

In less drastic conditions of dryness it is possible to detect, at potentials anodic to R_1, an irreversible oxidation peak O_3 which can be related to the oxidation of carbanion TH^-, formed by protonation of T^{2-}, with the regeneration of substrate T[21,22] as evidenced by the steady-state voltammograms of Figure 2. In detail, the oxidation of TH^- can be viewed as a three-step mechanism [reaction (4)].

$$TH^- \underset{}{\overset{-e}{\rightleftharpoons}} TH^\bullet \xrightarrow{-H^+} T^{-\bullet} \xrightarrow[\text{and/or } + TH\cdot]{-e} T \qquad (4)$$

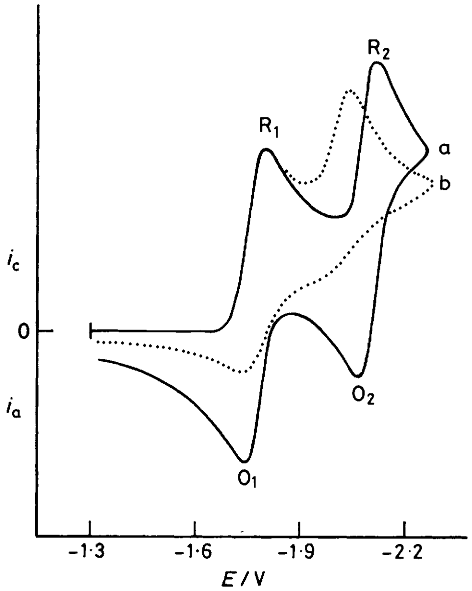

FIGURE 1 Cyclic voltammograms of T (1.0mM) at 10 °C, with (a) and without (b) activated alumina. Voltage sweep rate 0.25 V s^{-1}

Hence, according to the voltammetric theory,[23] the peak potential of O_3 is cathodic to the corresponding reversible potential of the $TH^\bullet$–TH^- pair.

O_3 disappears when the concentration of proton donor is slightly increased; in this case we must have quantitative protonation of TH^- to TH_2. Under the same conditions, however, the radical anion $T^{-\bullet}$ is stable; in fact R_1 remains completely reversible. Consequently, it can be said that for this substrate, as seen for other compounds, the carbanion is a stronger base than the anion radical.[12,22]

The voltammetric behaviour in the presence of added

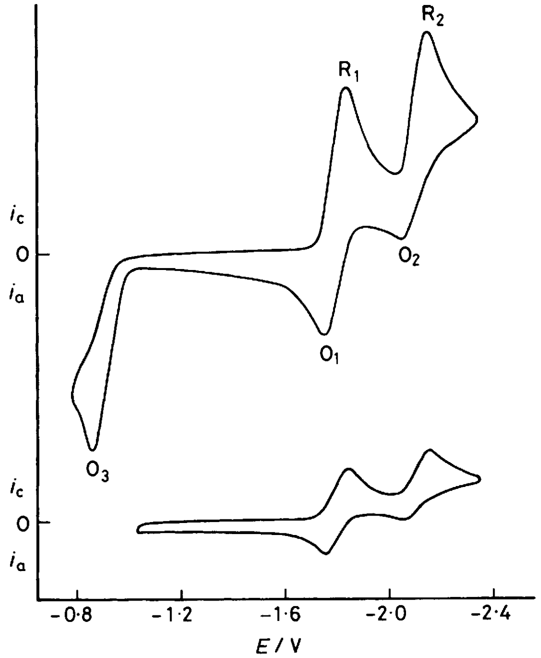

FIGURE 2 Steady-state voltammograms of T (1.0mM) at −25 °C. Voltage sweep rate 6 V s^{-1}

water points out that the first reduction peak becomes chemically irreversible. For example, at room temperature with [T] 10^{-3}M, the kinetic effect on R_1 is detected at a low scan rate (0.1 V s^{-1}) when the water concentration is *ca.* 10^{-2}M. Further addition of the proton donor causes an increase of R_1 in connection with a decrease of R_2 and O_1 showing how some radical anion has decayed in the time scale of the experiment before its reduction to dianion or oxidation to substrate.

Electrolysis.—Whenever the system is carefully pretreated in order to remove proton donor impurities, exhaustive controlled-potential electrolysis at the first polarographic reduction wave at low temperatures ($T < 0$ °C) takes 1 F mol^{-1} and leads to the formation of a very stable radical anion. The height of its oxidation wave decreases very slowly with half-regeneration of the first reduction wave. The half-regeneration of the substrate and the nature of the reduction product, triphenylethane, are consistent with the general stoicheiometry of radical-anion decay [see equation (1)].

Exhaustive electrolysis at the second reduction wave takes 2 F mol^{-1} but even in the dryest conditions realized the dianion did not accumulate according to its high reactivity towards any available proton source, the solvent–electrolyte system included. At similar potentials of the voltammetric peak O_3, we observed an oxidation wave of moderate stability that we can ascribe to the oxidation of carbanion TH^-.

In the presence of water exhaustive controlled-potential electrolysis of T at either the first or second reduction waves leads to the contemporary disappearance of both the waves and takes 2 F mol^{-1}. Triphenylethane is formed quantitatively.

Homogeneous Kinetics.—In order to elucidate the mechanism of decay of triphenylethylene radical anion in DMF in the presence of water, we carried out a kinetic study by the amperometric method. Kinetics of protonation were driven in the presence of parent hydrocarbon T and proton donor H_2O both in excess, so that their concentrations were nearly constant during the overall reaction allowing the pseudo-second-order treatment. Several kinetic runs were carried out at different reactant concentrations with T −30 °C.

The disappearance of $T^{-\bullet}$ was found to be second-order in its concentration over at least three half-lives. The values of the pseudo-second-order rate constant k_{II} depend on water and parent substrate concentrations, the reaction being retarded by T and speeded up by H_2O.

The kinetic results combined with the stoicheiometry of the radical anion decay [equation (1)] suggest, as in other protonation kinetics,[4,5,10] the hypothesis of the disproportionation mechanism (5)—(7) which, in the steady-state

$$2T^{-\bullet} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} T + T^{2-} \qquad (5)$$

$$T^{2-} + H_2O \xrightarrow{k_p} TH^- + OH^- \qquad (6)$$

$$TH^- + H_2O \longrightarrow TH_2 + OH^- \qquad (7)$$

assumption for the reactive dianion, leads to the rate law (8) and hence (9).

$$-\frac{d[T^{-\bullet}]}{dt} = \frac{2k_f k_p[H_2O]}{k_b[T] + k_p[H_2O]}[T^{-\bullet}]^2 = k_{II}[T^{-\bullet}]^2 \qquad (8)$$

$$\frac{1}{k_{II}} = \frac{1}{2k_f} + \frac{[T]}{2K_d k_p[H_2O]} \qquad (9)$$

The dependence of the values of k_{II} on the concentrations of substrate and water agrees well with equation (9). In fact, the plots of the reciprocal of k_{II} *vs.* [T] at given water concentrations are linear in the concentration range investigated with the same non-zero intercept, within experimental error (Figure 3). This intercept is related to the forward disproportionation rate constant k_f in accord with equation (9). The water dependence of k_{II} was tested by plotting $1/k_{II}$ against [T]/[H_2O] (Figure 4). As predicted by equation (9), a linear correlation was verified; the scatter of the experimental points is explained by the high sensitivity of these protonation reactions to air, moisture,

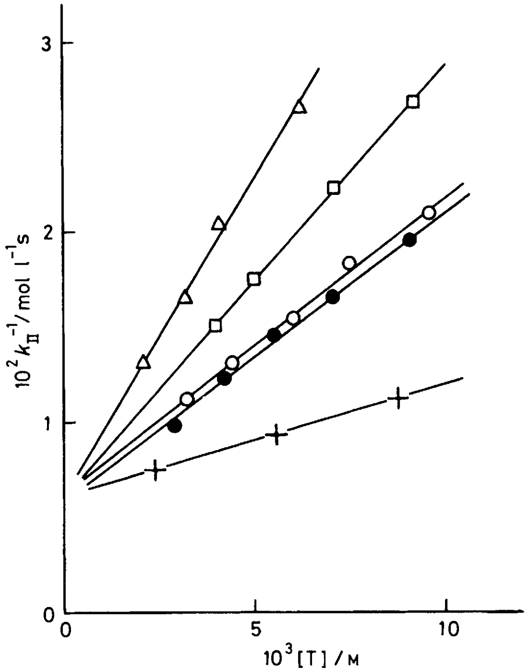

FIGURE 3 Plots of the reciprocal of k_{II} *versus* [T]. T −30.0 °C. Water concentration: 0.095M (△), 0.15M (□), 0.18M (○), 0.19M (●), 0.52M (+)

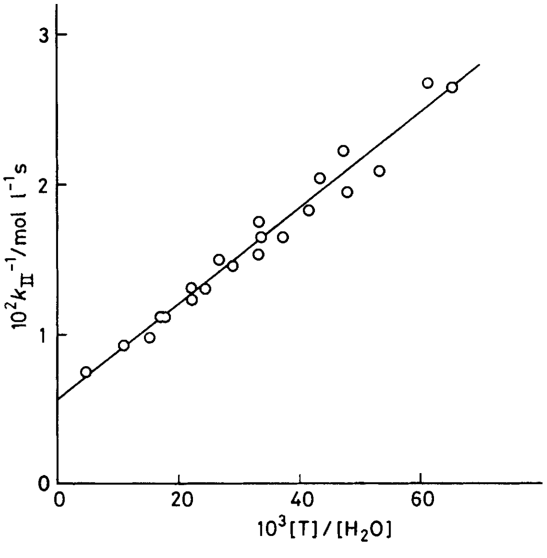

FIGURE 4 Plot of $1/k_{II}$ *versus* [T]/[H_2O]. T −30.0 °C

and impurities.[3,4] From the slope and the K_d value previously obtained we calculated the protonation rate constant k_p. The possible effect of the conjugated base OH^- was tested by carrying out some kinetic runs with different $[OH^-]$. The hydroxide ions were produced *in situ* by pre-electrolysis of known amounts of substrate at given water concentrations. The extent of the electrolysis was chosen every time in order to reach, at the end of the decay, the same fixed values of [T] and $[H_2O]$. The $[OH^-]$ was varied in a range of approximately one order of magnitude up to *ca.* 0.07M. The k_{II} values were constant within the experimental error. Kinetic runs were repeated at different temperatures. Equilibrium and rate constant values are listed in the Table.

Equilibrium and rate constant values [a] obtained from homogeneous or voltammetric measurements

T/°C	$10^7 K_d$	$10^{-3} k_f$/l mol^{-1} s^{-1}	$10^{-8} k_b$ [b]/l mol^{-1} s^{-1}	$10^{-6} k_p$ [c]/l mol^{-1} s^{-1}
−30.0	4.5	0.090 [c]	2.0	3.5
−25.1	5.8	0.14 [c]	2.4	4.6
−20.0	7.4	0.21 [c]	2.8	5.9
0.0	18	0.85	4.8	
10.4	26	1.8	6.9	
25.0	44	4.7	11	
40.4	71 [d]	13	18	
58.6	120 [d]	27	23	

[a] The k_f and the k_p values are reproducible to within ±10 and 6%, respectively. [b] Calculated from the corresponding k_f and K_d values. [c] Obtained from homogeneous kinetics. [d] Extrapolated data.

Voltammetric Kinetics.—The disproportionation mechanism requires that the pseudo-second-order rate constant k_{II} is independent of $[H_2O]$ and [T] when $k_p[H_2O] \gg k_b[T]$; with this condition the dianion protonation step is very fast relative to the comproportionation step, the disproportionation reaction becomes the rate-determining step, and the rate law (8) reduces to (10) which corresponds to the irreversible disproportionation mechanism. Thus direct measurement of k_f is possible.

$$-d[T^{-\bullet}]/dt = 2k_f[T^{-\bullet}]^2 \qquad (10)$$

This situation cannot be detected by the amperometric method in homogeneous conditions because of the limit set by the rather high values of k_f. On the other hand, cyclic voltammetry can be a useful technique to analyse under these conditions.[20,24] The nature of our system and the relatively high rates of reaction required by this transient technique forced us to work at temperatures higher than 0 °C.

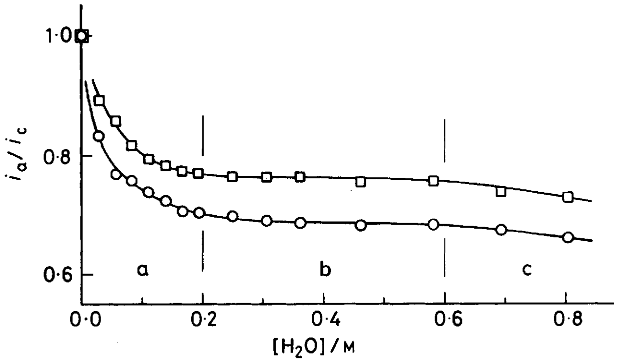

FIGURE 5 Dependence of the ratio i_a/i_c of the first step on water concentration. T 58.6 °C. Voltage sweep rate: 1.5 V s^{-1} (○), 2.5 V s^{-1} (□). [T] 1.0mM

In order to evaluate the conditions in which the disproportionation can be considered irreversible, we carried out a preliminary study on the dependence of the ratio (i_a/i_c) of anodic to cathodic peak currents of the first step on water concentration, at constant scan rate and temperature. Typical plots are reported in Figure 5. In the absence of water the ratio is unitary and decreases with additions of the proton donor (zone a) up to a constant value within experimental error. The plateau (zone b) leads to the conclusion that, under these conditions, the water concentration does not enter into the kinetic law as required by irreversible disproportionation. At higher concentrations (zone c) the ratio i_a/i_c begins a gradual decrease.

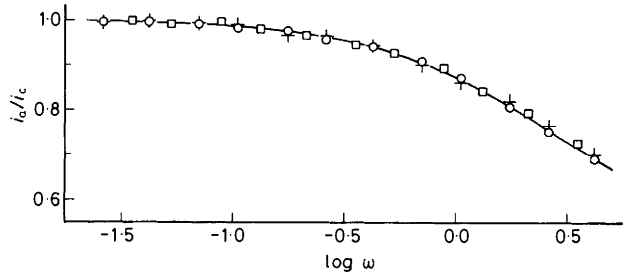

FIGURE 6 Plot of the ratio i_a/i_c *versus* log ω at 25.0 °C. The theoretical working curve for the irreversible disproportionation mechanism (solid line) and log ω are defined in ref. 20. The best fitting is obtained for k_f 4.7 × 10^3 l mol^{-1} s^{-1}. [T] 1.0mM, $[H_2O]$ 0.20M (○), 0.40M (+). [T] 0.5mM, $[H_2O]$ 0.40M (□)

The system was then thoroughly studied and the voltammetric analysis was carried out at temperatures ranging from 0 to 60 °C; water concentrations were chosen in zone b. Among the voltammetric diagnostic criteria, only the

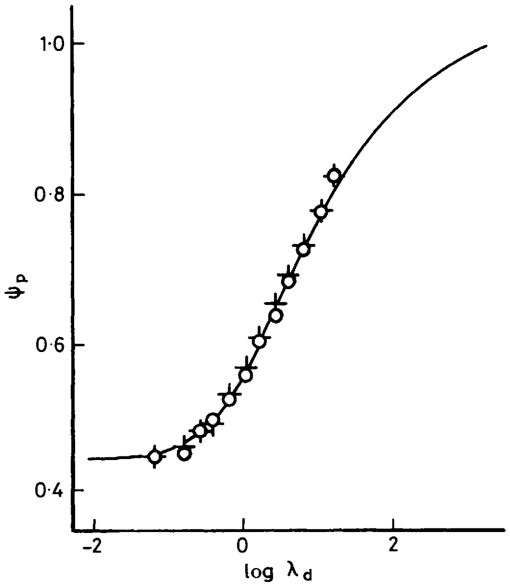

FIGURE 7 Plot of the peak-current function ψ_p *versus* log λ_d at 58.6 °C. The theoretical working curve for the irreversible disproportionation mechanism (solid line) and log λ_d are defined in ref. 23. The best fitting is for k_f 2.7 × 10^4 l mol^{-1} s^{-1}. [T] 1.0mM. Water concentration: 0.25M (○), 0.36M (+)

ratio i_a/i_c was employed over the full range of temperatures because of its greater sensitivity towards slow reactions; the peak-current function (ψ_p) proved to be equally useful at $T > 40$ °C. The peak-potential criterion was not used quantitatively owing to the particular kinetic zones covered by our system.[24]

Voltammetric data were obtained for each temperature at several scan rates and different substrate and water concentrations; the experimental values fit fairly well on the theoretical working curves calculated for the proposed mechanism [20,23] as can be seen in Figures 6 and 7. The rate constants k_f obtained are reported in the Table. In particular, the effect of the depolarizer concentration on the voltammetric behaviour strongly supports the second-order kinetics predicted by the irreversible disproportionation mechanism (see Figure 6).

The k_f values obtained by both homogeneous and voltammetric kinetic measurements are reported in an Arrhenius plot in Figure 8.

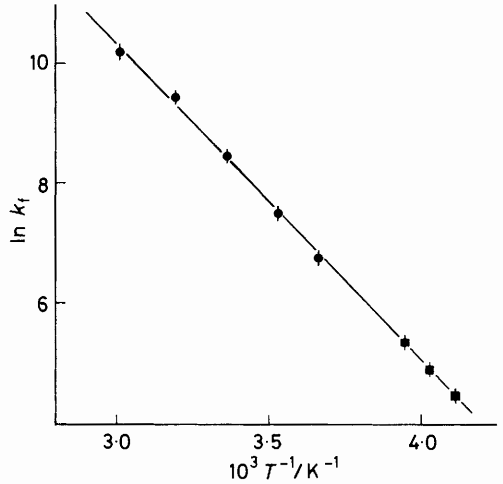

FIGURE 8 Arrhenius plot of the disproportionation-rate constant of $T^{-\bullet}$. Homogeneous data (■); voltammetric data (●). Activation energy 10.5 ± 0.6 kcal mol^{-1}

DISCUSSION

Some reactions of radical ions are reported to follow second-order rate laws in the radical-ion concentration while being retarded by the parent hydrocarbon.[25] Our experimental results support the disproportionation mechanism; however, the regeneration mechanism can compete according to the sequence (11)—(13).

$$T^{-\bullet} + H_2O \overset{K_{11}}{\rightleftarrows} TH^{\bullet} + OH^- \qquad (11)$$

$$TH^{\bullet} + T^{-\bullet} \underset{k_{-12}}{\overset{k_{12}}{\rightleftarrows}} TH^- + T \qquad (12)$$

$$TH^- + H_2O \xrightarrow{k_{13}} TH_2 + OH^- \qquad (13)$$

Also in this case, second-order kinetics in the radical-anion concentration and the inhibiting effect by T are predicted.[9] The analogous equation (14) to (9) can be obtained only with the hypothesis of a stationary-state concentration for the species TH^-.

$$\frac{1}{k_{II}} = \frac{[OH^-]}{2k_{12}K_{11}[H_2O]} + \frac{[OH^-]}{2k_{13}K_{11}K_{12}[H_2O]^2}\cdot[T] \quad (14)$$

For our substrate, however, the regeneration mechanism can be disregarded as will be explained in the following discussion. (i) While the regeneration mechanism predicts an intercept of the $1/k_{II}$ *versus* [T] plot which is dependent on $[H_2O]$ [equation (14)], the disproportionation mechanism leads to an independent one [equation (9)]; the latter is indeed the case as can be seen in Figure 3. (ii) The slope of the $1/k_{II}$ *versus* [T] plot, in the range considered, is inversely proportional to the first power of water concentration while the regeneration mechanism predicts an inverse-second-power dependence. (iii) According to the disproportionation mechanism, kinetic results are independent of the hydroxide ions formed or those ultimately present in the reaction medium. (iv) In agreement with the behaviour of the oxidation of carbanion TH^- (peak $O_{3'}$) the difference in peak potentials between O_3 and O_1 (>0.9 V at −30 °C) allows a rough *minimum* estimation of the equilibrium constant of the electron transfer (12), that is $K_{12} > 10^{18}$. In the likely hypothesis that k_{12} is a diffusional-rate constant,[26] k_{-12} must have a value lower than 10^{-8} l mol^{-1} s^{-1}. Moreover, if we now consider that TH^- is a species with a relatively high basicity and that in our homogeneous conditions $[H_2O] > 10[T]$, it is clear how $k_{-12}[T] \ll k_{13}[H_2O]$ and, therefore, how step (12) is decisively irreversible. Hence, the observed inhibiting effect by T cannot be explained.

An alternative mechanism, *via* a radical-anion–water complex, with a reaction scheme analogous to that reported by Parker [25,27] for radical cations, can be disregarded on the basis of the expected dependence of the intercept of $1/k_{II}$ *versus* [T] on water concentration.

The voltammetric evidence supports the irreversible disproportionation mechanism allowing a direct determination of the corresponding rate constant k_f. The difference between homogeneous and voltammetric kinetic results consists in the shift of the rate law from equation (8) to (10), owing to a higher weight acquired by the term $k_p[H_2O]$ with respect to $k_b[T]$. In fact, if we consider typical concentrations of T (1.0mM) and H_2O (0.3M) employed in the voltammetric measurements, and the values of k_b and k_p obtained from homogeneous kinetics (see Table), the ratio $k_p[H_2O]/k_b[T]$ is 5.2 and 6.3 at −30 and −20 °C, respectively. This increase is due to a slightly higher temperature dependence of k_p with respect to k_b. Thus, a higher ratio can be expected in the temperature range of the voltammetric kinetics. Moreover, if we consider that throughout the reaction layer the actual concentration of T is lower than its analytical value, $k_b[T]$ can be considered negligible with respect to $k_p[H_2O]$, according to the experimental results.

A priori, the regeneration or the complexation mechanisms could be operating in the conditions in which the voltammetric experiments were carried out.* It should be noticed, however, that in both cases water enters in

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* In particular conditions, both regeneration and complexation mechanisms can be described by the same voltammetric working curves of the irreversible disproportionation mechanism.[23]

the first step. As a consequence, the reaction rate should depend on [H_2O] for any value of the latter. This is in contrast with our results which show that, in a wide concentration range (zone b), both i_a/i_c and ψ_p are practically independent of [H_2O].

The disproportionation mechanism is therefore the only one supported by both homogeneous and voltammetric evidence. Furthermore, the Arrhenius plot of the disproportionation rate constant k_f (Figure 8) shows that the two sets of data agree fairly well.

The proposed mechanism is supported even by the consistency of the rate constant values obtained. The comproportionation step is nearly diffusional (k_b 1.1×10^9 l mol^{-1} s^{-1} at 25 °C) as verified for similar electron-transfer reactions.[10,26] The k_p values can be compared with those of the dianions of aromatic compounds like anthracene and perylene; typical values [10,28] range from *ca.* 10^5—10^7 l mol^{-1} s^{-1} and thus our data agree fairly well. In the case of the protonation of alkaline salts of the anthracene dianion, nearly diffusional rate constant values are observed; indeed, this is one of the experimental results which led to the conclusion that the reactivity of ion pairs increases with their tightness and thus localization of charge.[4-6] The bulky Bu_4N^+ counterions employed in the electrolytic medium of our system should prevent the formation of tight aggregates with the dianions, yielding only weak interactions.[21] Thus, it seems reasonable to observe high but not excessive reactivity of T^{2-} dianions. The protonation rate constants reported in this paper were calculated from the slopes of the $1/k_{II}$ plots, on the basis of the K_d values obtained in anhydrous conditions. This procedure may be considered incorrect; however, if we note that the linearity of the plot $1/k_{II}$ *versus* [T]/[H_2O] is relatively good (Figure 4), we can conclude that the K_d values, and consequently the k_p values, are unaffected by the presence of water, at least in the concentration range investigated.

The irreversibility of the disproportionation with the appropriate conditions gives powerful support for the mechanism. To date, disproportionation mechanisms of radical ions have failed to be observed in the shift from equilibrium conditions to the irreversibility caused by a very fast reaction of the dianion or dication with the reactant. For instance, the shift was hindered either by the occurrence of a competitive mechanism,[25] or by the breakdown of the simple disproportionation mechanism at high concentrations of the proton donor, owing to the increasing contribution to the protonation reaction of intermediate ion-cluster species.[4,5] In this light, decay of $T^{-\cdot}$ appears to be a clear example of an uncomplicated protonation mechanism *via* a dianion.

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