ELECTROCHEMICAL REDUCTION OF 1-HALO-2-BUTENES IN DIMETHYLFORMAMIDE

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Received November 10, 1992
Accepted May 15, 1993

The electrochemical reduction of 1-bromo-2-butene and 1-chloro-2-butene in DMF at a Hg electrode has been studied by polarography, cyclic voltammetry (CV), a rotating ring-disk electrode and controlled-potential coulometry. A CV study using a gold electrode has also been carried out for these compounds to identify the detected intermediates. Two consecutive one-electron reduction processes are found for 1-bromo-2-butene in polarography and in CV using a Hg electrode. The first process is initiated by the irreversible one-electron cleavage of the carbon–bromo bond to give the allyl radical and Br^-, which is the rate-determining step. The second one follows a first-order EC mechanism, being initiated by generation of the allylmercury anion via a one-electron reduction of the allylmercury radical, previously formed by reaction of the allyl radical with Hg. A single irreversible two-electron process is found for 1-chloro-2-butene under all voltammetric conditions and for both compounds in CV using a gold electrode. Additional anodic peaks detected in CV, as well as anodic waves found at the rotating Hg ring electrode, are ascribed to oxidation of the allylmercury anion and the allyl anion.

The electrochemical reduction of organic halogen compounds in non-aqueous media has been extensively investigated[1]. It is well established that electroreduction of aliphatic monohalides (RX) involves cleavage of the carbon–halogen bond yielding hydrocarbons (RH) and/or dimers (R–R) as main products, along with the free halide anions (X^-). It is widely accepted that the carbanion R^- is usually formed by a one-electron reduction of the radical intermediate $R^\bullet$, previously generated from the initial one-electron cleavage of the carbon–halogen bond. Further reaction of R^- with a proton donor present in the medium leads to RH.

Although voltammetric reduction for most organic monohalides shows a single two-electron process following the above-indicated mechanism, some controversial results have been reported for the electroreduction of allyl halides on mercury[2–6]. Thus, Petrovich and Baizer[2] observed two consecutive one-electron polarographic waves for the reduction of 1-bromo-2-propene in dimethylsulfoxide (DMSO) and dimethylformamide (DMF) containing tetraethylammonium perchlorate (TEAP) as background electrolyte, whereas 1-chloro-2-propene exhibited a single two-electron polarographic reduction wave. The findings for allyl bromide were ascribed to stepwise reduction to allyl radical followed by reversible reduction of the radical to the carbanion. In addition, Baizer and Chruma[3] found that electrolysis of each of these 1-halo-2-propenes (Allyl–X) in DMF with tetraethylammonium bromide yields a mixture of propene and 1,5-hexadiene at a Hg cathode. These products were assumed to be formed from the respective reaction of the carbanion with a proton donor or with the starting material, although the authors also considered that the diolefin can proceed from thermic decomposition of the electrode product diallylmercury $(Allyl)_2Hg$.

On the other hand, Bard and Merz[4] reinvestigated the electroreduction of 1-bromo-2-propene and other allyl bromides in acetonitrile containing tetrabutylammonium perchlorate (TBAP) by cyclic voltammetry (CV) at scan rates, v, between $0.1 - 0.5\ V\ s^{-1}$. In a hanging mercury drop electrode, 1-bromo-2-propene displayed only a reduction peak for $v \geq 0.2\ V\ s^{-1}$, whereas as lower scan rates a smaller peak appeared at more negative potentials, which was associated to the reduction of $(Allyl)_2Hg$ to the carbanion $Allyl^-$. These authors proposed that $(Allyl)_2Hg$ is generated by dimerization of the initially electrogenerated radical $Allyl–Hg^{\bullet}$. In contrast to Baizer et al.[2,3], Bard and Merz concluded that 1-bromo-2-propene is reduced via a single two-electron electrode reaction and the reduction of radical to anion can not be seen as a separate step.

The polarographic reduction of 1-bromo-2-butene and other allyl halides in dioxane–water mixtures was studied by Kirrman and Kleine-Peter[5,6]. These authors observed a similar behaviour for 1-bromo-2-propene and 1-bromo-2-butene and suggested a general reduction mechanism involving allyl and diallylmercury derivatives. Furthermore, it has been proposed[3,5] that diolefins are formed as reduction products via thermic decomposition of diallylmercury intermediates.

To gain a better understanding of the mechanism of the electrochemical reduction of allyl halides in non-aqueous media, we have undertaken a investigation of the electroreduction of 1-bromo-2-butene and 1-chloro-2-butene in DMF on a mercury electrode by means of polarography, CV, a rotating ring-disk electrode (RRDE) and controlled-potential coulometry. Comparative cyclic voltammograms for both compounds at a gold electrode have also been carried out to identify the intermediates formed in their reduction processes. The results of our study are reported herein.

EXPERIMENTAL

1-Bromo-2-butene (Fluka, purum) and 1-chloro-2-butene (Fluka, purum) were tridistilled at 103 – 105 °C and at 83 – 85 °C, respectively, at atmospheric pressure, before being used in the electrochemical experiments. The purity of these compounds was checked from ^1H NMR spectra (Perkin–Elmer R12 60 MHz spectrometer). These spectra revealed that each of such compounds was composed by a mixture of its isomers cis and trans, the latter one being the predominant form. DMF (Merck) was purified as described previously[7]. Tetraethylammonium perchlorate (Carlo Erba, polarographic grade) and tetrabutylammonium perchlorate (Fluka, purum) were dried under vacuum at

60 °C for 24 h. Tetrabutylammonium iodide (TBAI) supplied by Fluka, puriss. p.a., was recrystallized from water and vacuum dried at 60 °C for 24 h. Phenol (Merck, A.R. grade) was used as received.

Polarographic measurement were performed with an Amel 463 multipolarograph. Cyclic voltammetric measurements were carried out with an Amel 551/SU potentiostat, a Tacussel GSAP signal generator and a Philips 8120 X-Y recorder. Rotating ring-disk electrode (RRDE) measurements were carried out with a Tacussel BI-PAD potentiostat, equipped with the same signal generator and X-Y recorder as used in CV experiments. All potentials were corrected for ohmic drop. Controlled-potential coulometries were performed with an Amel 555A potentiostat equipped with an Amel 721 current integrator.

Polarographic experiments were conducted in a conventional three-electrode cell of 75 cm^3 capacity. CV and RRDE experiments were carried out with a Tacussel XLRC 10 cell of 200 cm^3 capacity. All voltammetric experiments were performed under nitrogen atmosphere. The temperature was always kept at 25.0 °C. An Ag/AgI, TBAI (0.1 mol dm^{-3} in DMF) was used as reference electrode and a Pt wire as counter-electrode. The flow rate, m, of the dropping mercury electrode employed in polarography was of 1.50 mg s^{-1} in DMF with 0.1 mol dm^{-3} TEAP, on open circuit at a mercury height of 35 cm. In cyclic voltammetry, the working electrode was a platinum sphere, sealed into glass, electrolytically covered by a thin layer of silver and then amalgamated by dipping it in mercury. The surface of this electrode of area 0.12 cm^2 was renewed, before each experiment, by dipping in mercury. Some CV experiments were also carried out using a polished gold electrode of area 0.032 cm^2 as working electrode. In RRDE experiments, the working electrode was a Tacussel EAD ring-disk electrode, with a disk radius of 0.20 cm and ring radii of 0.22 cm (internal) and 0.24 cm (external). The platinum of both ring and disk electrodes was coated with mercury before each experiment, following the procedure described in ref.[8]. The collection coefficient, N, of the resulting rotating mercury ring-disk electrode was determined to be 0.20 ± 0.01 from the ratio between the limiting currents of ring and disk waves recorded for the reversible one-electron system formed by fluorenone and its radical anion.

Solutions of concentration, c, between 0.2 and 1.0 mmol dm^{-3} of each substrate in DMF with 0.1 mol dm^{-3} TEAP as background electrolyte and drop times, t, between 1.0 and 4.0 s were used in polarography. Drop times were regulated with a Tacussel GCMS hammer. Scan rates, v, between 10 and 280 mV s^{-1} and concentrations 1.0 – 5.0 mmol dm^{-3} of substrate in DMF containing 0.1 mol dm^{-3} TEAP were employed in cyclic voltammetry. Several CV experiments were also carried out using 0.1 mol dm^{-3} TBAP as background electrolyte. Phenol (ϕOH) was employed as proton donor under polarographic and CV conditions. Rotating speeds, ω, between 100 and 6 000 r.p.m. and a concentration 1.0 mmol dm^{-3} of substrate in DMF with 0.1 mol dm^{-3} TEAP were employed in the RRDE experiments. The rotating speed of the RRDE was controlled by an Asservitex 10, 000, from Tacussel.

Controlled-potential electrolyses were conducted in a H-cell under nitrogen. The temperature was also kept at 25.0 °C. A mercury pool, magnetically stirred, of area ca 20 cm^2 was used as cathode, an Ag/AgI as reference electrode and a grafite rod as anode. Volumes of 150 and 50 cm^3 of DMF containing 0.1 mol dm^{-3} TEAP were introduced in the cathodic and anodic compartments, respectively. The catholyte was then pre-electrolyzed at the chosen potential to determine the correction for residual current. After addition of 1 mmol of substrate, exhaustive electrolysis was carried out. The number of coulombs passed was corrected considering the residual current. The amount of halide ion liberated for each substrate was gravimetrically determined from silver halide obtained by adding an excess of $AgNO_3$ dissolved in 5 cm^3 of water to the electrolyzed solutions.

RESULTS AND DISCUSSION

Polarography

Table I summarizes polarographic results for the reduction of 1.0 mmol dm^{-3} 1-halo-2-butenes in DMF containing 0.1 mol dm^{-3} TEAP, without and with phenol as proton donor. In all media, 1-bromo-2-butene always displayed two consecutive reduction waves (I and II) of equal limiting current, I_l, whereas 1-chloro-2-butene exhibited a single reduction wave. For each wave, good linear plots of log I_l vs log c and log I_l vs log t, with respective slopes close to 1.0 and 0.19, were obtained in all solutions, indicating that it is always diffusion controlled.

As can be seen in Table I, values of 2.00 and 2.06 μA dm^3 $s^{1/2}$ $mmol^{-1}$ $mg^{-2/3}$ are determined for the respective diffusion-current constants, I_d, of waves I and II of 1-bromo-2-butene in the absence of phenol. Under these conditions, 1-chloro-2-butene has an I_d value of 3.39 μA dm^3 $s^{1/2}$ $mmol^{-1}$ $mg^{-2/3}$. Addition of phenol does not change practically the I_d value for both waves of 1-bromo-2-butene, but causes a strong increase in the I_d value of the wave of 1-chloro-2-butene, which gets a constant value of 4.42 μA dm^3 $s^{1/2}$ $mmol^{-1}$ $mg^{-2/3}$ when the ratio of $c_{\phi OH}/c$ is higher than 3. Taking into account that I_d values of 4.00 and 3.45 μA dm^3 $s^{1/2}$ $mmol^{-1}$ $mg^{-2/3}$ have been obtained for the respective single irreversible two-electron reduction polarographic waves of *trans*-1,4-dibromo-2-butene and *trans*-1,4-dichloro-2-butene in DMF with 0.1 mol dm^{-3} TEAP (ref.[9]), it can be inferred that under the investigated experimental conditions,

TABLE I
Polarographic results for the reduction of 1-halo-2-butenes in DMF containing 0.1 mol dm^{-3} TEAP. Flow rate 1.50 mg s^{-1}, drop time 4.0 s, substrate concentration 1.0 mmol dm^{-3} and temperature 25.0 °C

Compound	Wave	$c_{\phi OH}$ mmol dm^{-3}	$E_{1/2}$, V [a]	I_l, μA	I_d [b]	αn [c]	n [d]
1-Bromo-2-butene	I	–	−0.70	3.30	2.00	0.34	
		4.0	−0.70	3.40	2.06	0.34	
	II	–	−1.03	3.42	2.07		1.01
		4.0	−1.03	3.61	2.19		0.99
1-Chloro-2-butene		–	−1.65	5.59	3.39	0.19	
		4.0	−1.67	7.29	4.42	0.17	

[a] E vs Ag/AgI, TBAI (0.1 mol dm^{-3} in DMF). [b] $I_d = I_l/c\, m^{2/3}\, t^{1/6}$. [c] Determined from logarithmic analysis considering an irreversible charge transfer reaction[10]. [d] Determined from logarithmic analysis considering a first-order EC mechanism[10].

1-bromo-2-butene undergoes two consecutive one-electron reduction reactions, whereas a single two-electron reduction process takes place for 1-chloro-2-butene.

The half-wave potential, $E_{1/2}$, for wave II of 1-bromo-2-butene was found to be independent of c, although it was shifted to less negative potentials with increasing $\log t$ by some 30 mV per decade, as expected for a first-order EC mechanism[10]. For wave I of 1-bromo-2-butene and for the single wave of 1-chloro-2-butene, the corresponding half-wave potential was also c-independent and showed a variation with $\log t$ higher than 100 mV per decade, according to the behaviour expected for irreversible transfer reactions[10]. Under the experimental conditions of Table I there is a difference of 0.33 V between the $E_{1/2}$ values of both waves of 1-bromo-2-butene. A similar $E_{1/2}$ difference of 0.32 V has also been reported by Petrovich and Baizer[2] for the two consecutive one-electron reduction polarographic waves of 1-bromo-2-propene in DMSO. Table I also shows that the reduction of 1-chloro-2-butene occurs at more negative potentials than that of 1-bromo-2-butene, consistent with the greatest ease to break the C–Br bond owing to its lower energy[1].

The logarithmic analysis of each wave was carried out considering the theoretical equations for first-order EC mechanisms and irreversible charge transfer processes[10]. Plots of E vs $\log |(I_l - I)/I|$ always showed good straight lines, with slopes practically independent of c and t. From these slopes, the corresponding αn product or the n value of each wave was determined. The results thus obtained are reported in the two last columns of Table I. As can be seen, low αn values were found for wave I of 1-bromo-2-butene and for the single wave of 1-chloro-2-butene, as expected for irreversible charge transfer reactions. In the case of wave II of 1-bromo-2-butene, an n value of about 1 was determined in all media (associated to slopes close to 60 mV per decade), indicating that it behaves as a first-order EC process.

Cyclic Voltammetry

Cyclic voltammograms corresponding to the reduction of 1.0 mmol dm^{-3} 1-bromo-2-butene in DMF containing 0.1 mol dm^{-3} TEAP at scan rates of 10 and 280 mV s^{-1} are shown in Fig. 1. On the cathodic portion of the voltage scan, two peaks, R_1 and R_2, were found. These peaks correspond to waves I and II obtained in polarography. Peak R_1 was completely irreversible at all scan rates. For $v < 50$ mV s^{-1} one anodic peak, O_2, associated to peak R_2 was also recorded (see Fig. 1*a*), even upon phenol addition. At higher scan rates, peaks R_1 and R_2 partially overlap and then, peak O_2 was ill-defined on the anodic scan (see Fig. 1*b*). A similar cyclic voltammetric behaviour observed for 1.0 mmol dm^{-3} 1-bromo-2-butene using TBA$^+$ as background cation, but in this case peak O_2 was not conspicuous. On the other hand, cyclic voltammograms of 1.0 mmol dm^{-3} 1-chloro-2-butene in DMF containing either 0.1 mol dm^{-3} TEAP or TBAP only displayed an irreversible cathodic peak, R_1, at all scan rates tested, which corresponds to its single reduction wave observed in polarography.

Values of cathodic peak potential, E_p^c, cathodic half-peak potential, $E_{p/2}^c$, cathodic peak current, I_p^c, and the slopes of the linear plots of log I_p^c vs log v and E_p^c (or $E_{p/2}^c$) vs –log v, for each reduction peak of 1.0 mmol dm^{-3} 1-halo-2-butenes in DMF using TEAP or TBAP as background electrolyte are given in Table II. Only reported CV parameters for 1-bromo-2-butene could be accurately determined due to the partial overlapping of its peaks R_1 and R_2. Addition of phenol to these solutions caused little effect upon these CV parameters. In fact, the main observed effect was an increase in I_p^c for peak R_1 of 1-chloro-2-butene, ca 15% at $c_{\phi OH}/c$ ratio > 3, similarly to results reported in Table I for I_l of its polarographic wave.

As can be seen in Table II, slopes close to 0.50 were obtained for the linear plots of log I_p^c vs log v corresponding to peak R_1 of both 1-halo-2-butenes, as well as the overall reduction peak of 1-bromo-2-butene, indicating[10] that all reduction processes are always diffusion controlled. When TEA^+ was used, E_p^c of peak R_2 of 1-bromo-2-butene was slightly shifted to more negative potentials with increasing log v by some 20 mV per decade, whereas the difference between the peak potentials of peaks O_2 and R_2 at v < 50 mV s^{-1} was found to be 0.11 V. These findings are consistent[10] with a quasi-reversible behaviour of the initial one-electron charge transfer reaction taking place in the second reduction process of this compound under CV conditions. On the other hand, good linear correlations between E_p^c (or $E_{p/2}^c$) and –log v with very large slopes were obtained for peaks R_1 of 1-bromo-2-butene and 1-chloro-2-butene in all media. This is the behaviour expected for irreversible charge transfer reactions[10], and hence assuming that these plots have slopes of $29.6/\alpha n$ mV per decade at 25.0 °C (ref.[11]), αn product values ca 0.3 and ca 0.2 for the respective peaks R_1 of 1-bromo-2-butene and

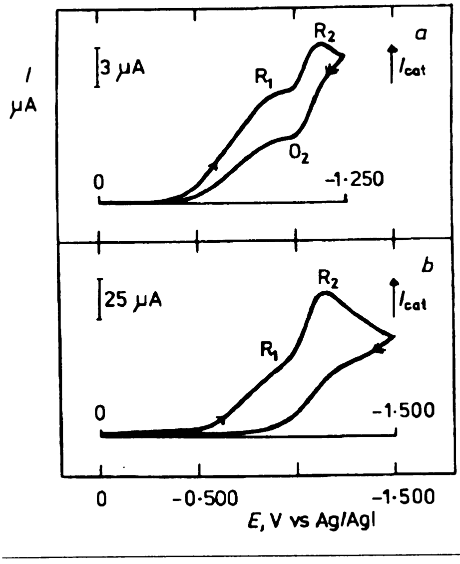

FIG. 1

Cyclic voltammograms of 1.0 mmol dm^{-3} 1-bromo-2-butene in DMF containing 0.1 mol dm^{-3} TEAP on a Hg cathode, at a scan rate of: *a* 10, *b* 280 mV s^{-1}. T = 25.0 °C. Starting potential (–>–) 0 V. Reversal potential (–>>–): *a* –1.250, *b* –1.500 V

1-chloro-2-butene were determined (see last column in Table II). These αn products are similar to those obtained for their corresponding polarographic waves, as stated above.

Table II also shows that the main effect upon all cathodic peaks when using TBA^+ instead TEA^+ as supporting cation is a displacement of E_p^c and $E_{p/2}^c$ at least 0.10 V to more negative potentials, pointing to a decrease in rate of charge transfer reactions[12]. Thus, peak R_2 behaved rather as an irreversible one-electron charge transfer process, since a slope of 50 mV per decade was determined for the E_p^c vs $-\log v$ plot, corresponding to αn value of 0.60 (see Table II). These results support that in the presence of TBA^+ the first charge transfer reaction of all observed process is the rate-determining step.

At substrate concentrations 5.0 mmol dm^{-3}, 1-halo-2-butenes displayed a complex behaviour in CV by varying v. Figure 2*a* shows a typical cyclic voltammogram recorded for 1-bromo-2-butene at 28 mV s^{-1}. As observed, the two reduction peaks R_1 and R_2 were well-defined under these conditions, although the height of peak R_1 (proportional to c and $v^{1/2}$) was apparently higher than that of peak R_2. With increasing v, the cathodic peak potential of peak R_2 remained almost constant, whereas E_p^c of peak R_1 was shifted to more negative potentials. This caused a partial overlapping between both reduction peaks from v = 100 mV s^{-1}. Simultaneously, a gradual increase in the peak current of peak R_2 with respect to that of peak R_1 occurred, up to reach similar I_p^c values for v > 250 mV s^{-1}, as can be seen in Fig. 2*b*. This CV behaviour for 1-bromo-2-butene

TABLE II

Cyclic voltammetric results for the reduction of 1-halo-2-butenes in DMF containing 0.1 mol dm^{-3} concentration of background electrolyte, on a Hg cathode. Substrate concentration 1.0 mmol dm^{-3} and temperature 25.0 °C

Compound	Background cation	Peak	E_p^c $V^{a,b}$	$E_{p/2}^c$ $V^{a,b}$	I_p^c μA^b	$\frac{\partial \log I_p^c}{\partial \log v}$	$\frac{\partial E_p^c \text{ (or } E_{p/2}^c)}{\partial \log v}$ mV per decade	αn
1-Bromo-2-butene	TEA^+	R_1	–	−0.74	26	0.52	100	0.30
		R_2	−1.11	–	38^c	0.58^c	20	–
	TBA^+	R_1	–	−0.85	21	0.51	100	0.30
		R_2	−1.23	–	32^c	0.47^c	50	0.60
1-Chloro-2-butene	TEA^+	R_1	−1.81	−1.57	49	0.53	120	0.25
	TBA^+	R_1	−2.07	−1.82	48	0.51	160	0.19

[a] E vs Ag/AgI, TBAI (0.1 mol dm^{-3} in DMF). [b] Values at a scan rate of 93 mV s^{-1}. [c] Overall process.

can be easily explained assuming that at low scan rates a certain amount of the electroactive species of peak R_2, generated in the first process (peak R_1) undergoes a chemical reaction and disappears prior its reduction, this causing the decrease in height of peak R_2. Time allowed a fast decrease of this chemical reaction with increasing v to 250 mV s^{-1}, whereupon it already does not take place and both reduction peaks reach equal height.

Cyclic voltammograms of 5.0 mmol dm^{-3} 1-bromo-2-butene in DMF with 0.1 mol dm^{-3} TEAP or TBAP at high scan rates also exhibited a set of additional peaks over the potential region between –0.15 and –0.50 V after reversing the scan at –1.25 V. As can be seen in Fig. 2*b*, on the anodic sweep a secondary oxidation peak, O_3, with a peak potential of ca –0.20 V was obtained, and after reversing again the scan at 0 V, two consecutive secondary reduction peaks, R_3 and R_4, with respective peak potentials of ca –0.30 V and –0.40 V were also found. In stirred solutions, these peaks decrease and even disappear, while peaks R_1 and R_2 increase. Note that additional peaks were not observed when the first scan was reversed at –1.0 V, i.e. at a potential corresponding to the first reduction process of 1-bromo-2-butene. On the other hand, after applying a potential of –1.25 V during 50 s, peak O_3 increases strongly in height, in the same way as peak R_3, which shows the shape of a typical adsorption peak and overlaps with R_4. All additional peaks disappear of cyclic voltammograms after phenol addition, sugges-

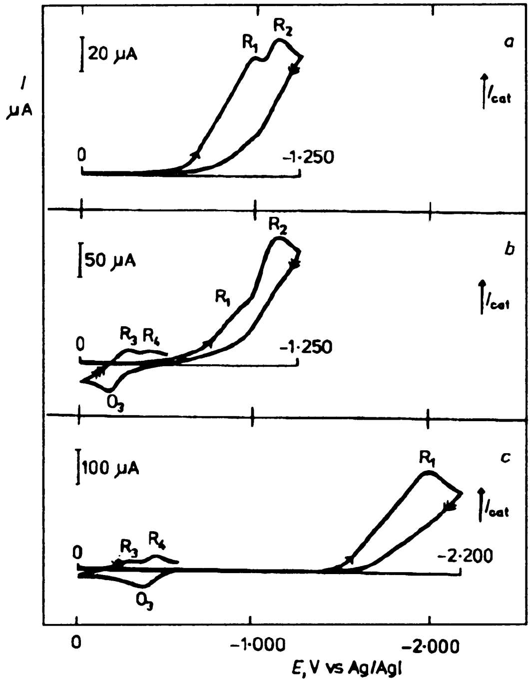

Fig. 2

Cyclic voltammograms of 5.0 mmol dm^{-3} 1-halo-2-butenes in DMF containing 0.1 mol dm^{-3} TEAP on a Hg cathode and at 25.0 °C. *a* 1-Bromo-2-butene at a scan rate of 28 mV s^{-1}, *b* 1-bromo-2-butene at a scan rate of 280 mV s^{-1}, *c* 1-chloro-2-butene at a scan rate of 280 mV s^{-1}. Starting potential (–>–) 0 V, first reversal potential (–>–>–): *a* –1.250, *b* –1.250, *c* –2.200 V, and second reversal potential (–>–>–>–) 0 V ting that peak O_3 is originated from oxidation of a basic species formed in the second process (peak R_2).

Cyclic voltammograms of 5.0 mmol dm^{-3} 1-chloro-2-butene in DMF always displayed the single irreversible two-electron diffusion-controlled reduction peak R_1 which peak current is proportional to c and $v^{1/2}$ under all tested experimental conditions, as shows Fig. 2*c*. At scan rates higher than 150 mV s^{-1}, secondary peaks O_3, R_3 and R_4, with respective peak potentials of ca –0.38 V, –0.30 V and –0.45 V were also recorded after reversing the scan at –2.20 V (see Fig. 2*c*). Peaks R_3 and R_4 were the same as obtained for 1-bromo-2-butene, whereas peak O_3 for 1-chloro-2-butene appeared at slightly more negative potentials than peak O_3 for 1-bromo-2-butene. Such peaks associated to the reduction of 1-chloro-2-butene are due to basic species generated in it, since they were not observed after phenol addition or during vigorous stirring of the solution.

To test whether the set of secondary peaks found for 1-halo-2-butenes on a Hg electrode are produced from the same basic species formed in their primary reduction peaks, several cyclic voltammograms of these substrates were carried out using a gold working electrode. A typical cyclic voltammogram for 1.0 mmol dm^{-3} 1-bromo-2-butene in DMF containing 0.1 mol dm^{-3} TEAP on a gold electrode is presented in Fig. 3. As observed, this compound only displayed a single irreversible two-electron diffusion-controlled reduction peak, R_1, appearing at more negative potentials than those found for its two reduction peaks on a Hg electrode (see Fig. 1). Figure 3 also shows the presence of a secondary reversible one-electron diffusion-controlled redox couple, O/R, with respective anodic and cathodic peak potentials of ca –0.33 and –0.40 V, i.e. it appears in the same potential region as secondary peaks recorded at the Hg electrode (see Fig. 2*b*). This couple disappeared either by stirring the solution or after phenol addition. The same secondary O/R couple was obtained in CV of 1-chloro-2-butene on gold, along with its primary irreversible reduction peak at ca –2.10 V. These findings suggest that the same species is oxidized in peak O of both compounds on gold as in peaks O_3 of 1-bromo-2-butene and 1-chloro-2-butene at Hg.

RRDE

Voltammograms of 1-bromo-2-butene and 1-chloro-2-butene at the Hg disk electrode of the RRDE displayed a single reduction wave over the whole ω range studied. However, the broadness and the shape of the allyl bromide wave suggest the merging of the two processes observed by polarography and CV. The half-wave potential, $E_{1/2}$, and the disk limiting current, I_D, obtained for each of these waves at different ω values are given in Table III. Waves are controlled by mass transport of substrate to the electrode provided that I_D is proportional to the square root of the rotating speed, according to Levich's criterion[13]. Since at each ω value waves for the two compounds have equal height (see Table III), it can be inferred that two electrons are involved in their reduction pathways. A gradual shift of $E_{1/2}$ of each wave to more negative potentials as long as ω increases can be observed in Table III, as expected for an irreversible charge transfer process[13]. Linear correlations between $E_{1/2}$ and log ω with slopes of ca −110 mV per decade were found for both waves. Assuming that these slopes are equal to $-29.6/\alpha n$ mV per decade, theoretically established for irreversible processes[10,13], an αn product of 0.26 was determined for the overall waves of 1-bromo-2-butene and 1-chloro-2-butene on the Hg disk electrode, a similar value to that obtained under polarographic conditions of wave I of 1-bromo-2-butene and the single wave of 1-chloro-2-butene (see Table I).

When either 1-bromo-2-butene or 1-chloro-2-butene was reduced at the disk of the RRDE, a single voltammetric wave corresponding to the oxidation of intermediates was also recorded at the Hg ring electrode when a constant ring potential of 0 V was applied. Figure 4 shows several ring current vs disk potential, E_D, voltammograms for 1.0 mmol dm^{-3} 1-bromo-2-butene in DMF containing 0.1 mol dm^{-3} TEAP, at different ω

TABLE III
RRDE results for the reduction of 1.0 mmol dm^{-3} 1-halo-2-butenes in DMF containing 0.1 mol dm^{-3} TEAP. Ring potential 0 V vs Ag/AgI and temperature 25.0 °C

ω, r.p.m.	$E_{1/2}$, V[a]	I_D, μA	I_R, μA	$N_k \cdot 10^3$
		1-Bromo-2-butene		
100	−1.39	53	1.3	25
200	−1.43	78	2.3	29
500	−1.49	133	4.0	30
1 000	−1.53	186	5.6	30
2 000	−1.56	265	7.8	29
4 000	−1.58	380	8.7	23
6 000	−1.59	460	11.3	25
		1-Chloro-2-butene		
100	−1.76	54	–	–
200	−1.81	80	–	–
500	−1.85	135	1.1	8
1 000	−1.89	190	1.6	8
2 000	−1.91	266	2.4	9
4 000	−1.95	370	3.3	9
6 000	−1.97	460	4.2	9

[a] E vs Ag/AgI, TBAI (0.1 mol dm^{-3} in DMF).

values and at a ring potential of 0 V. As observed, the anodic wave for 1-bromo-2-butene appeared at the ring from $E_D = -1.55$ V, whilst the reduction currents at the disk electrode arise at about −1.0 V, suggesting again severe overlapping of two consecutive processes. In addition, at $\omega > 200$ r.p.m. it shows a maximum (see Fig. 3) due to the oxidation of intermediates probably adsorbed on the Hg surface. However, the anodic wave for 1-chloro-2-butene appearing at the ring from $E_D = -1.80$ V reached a constant limiting current for all ω tested. The ring limiting current, I_R, and the corresponding collection coefficient, N_k, for the anodic wave of 1-halo-2-butenes recorded at a ring potential of 0 V are given in Table III. Comparing these N_k values with N (0.20), it can be deduced that ca 14% and 4% of intermediates generated in the respective reduction of 1-bromo-2-butene and 1-chloro-2-butene at the disk are reoxidized at the ring under our experimental conditions. On the other hand, the anodic waves found at the rotating Hg ring electrode disappeared after phenol addition, indicating that detected intermediates are basic species.

Controlled-Potential Coulometry

Several exhaustive controlled-potential reductions of 1-bromo-2-butene and 1-chloro-2-butene in DMF containing 0.1 mol dm^{-3} TEAP were carried out at potentials between −2.00 V and −2.20 V corresponding to the plateau of their overall polarographic reduction waves. Halide analysis of electrolyzed solutions showed complete liberation of halogen in all cases. The number of electrons transferred per reacting molecule (*n*

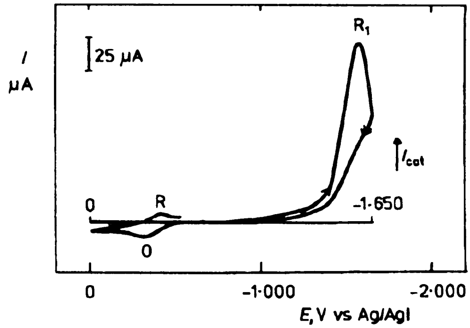

FIG. 3

Cyclic voltammograms of 1.0 mmol dm^{-3} 1-bromo-2-butene in DMF containing 0.1 mol dm^{-3} TEAP on a gold cathode, at a scan rate of 280 mV s^{-1} and at 25.0 °C. Starting potential (–>–) 0 V, first reversal potential (–>–>–) −1.650 V, and second reversal potential (–>–>–>–) 0 V

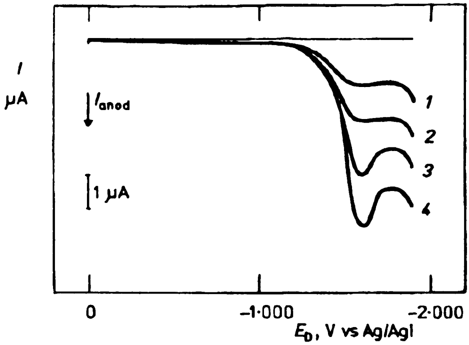

FIG. 4

Ring current vs disk potential voltammograms of 1.0 mmol dm^{-3} 1-bromo-2-butene in DMF containing 0.1 mol dm^{-3} TEAP on a rotating ring-disk mercury electrode, at a scan rate of 19 mV s^{-1} and at 25.0 °C. Rotating speed: *1* 100, *2* 200, *3* 500, *4* 1 000 r.p.m. Ring potential 0 V. Sweep rate 20 mV s^{-1}

value) after exhaustive electrolysis was found to be 1.02 for 1-bromo-2-butene and 1.63 for 1-chloro-2-butene. According to the previous literature, these results indicate that under electrolytic conditions 1-bromo-2-butene gives diolefins or the corresponding diallylmercury derivatives, since electrodimerization reactions yields $n = 1$ (refs[1,3]), whereas reduction of 1-chloro-2-butene leads to the formation of a mixture of diolefins and olefins (1-butene and 2-butene), these latter being the main products because an n value of 2 is required for their electrogeneration[1 – 4].

Reduction Mechanisms

Under polarographic and CV conditions, 1-bromo-2-butene in DMF containing 0.1 mol dm^{-3} TEAP or TBAP undergoes at the Hg electrode two consecutive one-electron reduction processes, as also observed by Petrovich and Baizer[2] for the polarographic reduction of 1-bromo-2-propene in DMSO. These authors have considered that these processes lead to the formation of the corresponding radical and of the carbanion, respectively. However, CV results for 1-bromo-2-butene show a more complex behaviour in which chemical reactions of the initially electrogenerated radical and chemical interactions between Hg and intermediates are involved. Our results are consistent with the presence of organomercury intermediates, as reported by other authors[4 – 6,14]. The fact that in controlled-potential electrolysis this compound yields an n value ca 1 suggests that its reduction pathway depends on the experimental conditions tested.

The intermediate anion radical which would result from the first electron transfer[1,4] has not been detected in our study, confirming the literature in the way that those radical anions, if exist, have a half-life lower than 10^{-3} s. Furthermore, the low α values obtained point to a transition state quite different of the reactants and, nowadays, most studies agree with a charge transfer concerted with C–X bond breaking for aliphatic halides[1,15].

All these considerations allow us to propose the following general reduction mechanism for 1-bromo-2-butene, denoted as BuBr, in DMF at the Hg electrode, consistent with voltammetric results in the presence and in the absence of phenol.

$$\mathrm{BuBr} + e \longrightarrow \mathrm{Bu}^{\bullet} + \mathrm{Br}^{-} \qquad (1)$$

$$\mathrm{Bu}^{\bullet} + \mathrm{Hg} \longrightarrow \mathrm{BuHg}^{\bullet} \qquad (2)$$

$$2\,\mathrm{BuHg}^{\bullet} \longrightarrow \mathrm{BuHgBu} + \mathrm{Hg} \qquad (3)$$

$$\mathrm{BuHgBu} \longrightarrow \mathrm{Bu{-}Bu} + \mathrm{Hg} \qquad (4)$$

$$BuHg^{\bullet} + e \rightleftharpoons BuHg^{-} \qquad (5)$$

$$BuHg^{-} \longrightarrow Bu^{-} + Hg \qquad (6)$$

$$Bu^{-} + H^{+} \longrightarrow BuH \qquad (7)$$

This pathway is initiated by an irreversible one-electron cleavage of the carbon–halogen bond of substrate to yield the allyl radical $Bu^{\bullet}$ and the anion Br^{-}. The allyl radical further reacts with a Hg atom of the electrode to form the corresponding allylmercury radical $BuHg^{\bullet}$, which subsequently either dimerizes in step 3 or is reduced in step 5. Decomposition of the diallylmercury BuHgBu formed in the coupling reaction of $BuHg^{\bullet}$ gives the diolefin Bu–Bu. The electrogenerated allylmercury anion $BuHg^{-}$ via a one-electron reduction of $BuHg^{\bullet}$ further decomposes to the anion Bu^{-}, which is finally protonated in step (*7*) to yield the olefin RH. The little effect of phenol upon the kinetic parameters of the reduction processes of 1-bromo-2-butene can be easily explained from this mechanism, since only Bu^{-} is protonated in step (*7*). In the absence of phenol, the proper tetraalkylammonium ion of the supporting electrolyte acts as source of protons via Hofmann degradation[12,14,16] and the rate of step (*7*) must be smaller.

According to this mechanism, two consecutive one-electron reduction processes take place for 1-bromo-2-butene since reduction potentials of $BuHg^{\bullet}$ are more negative than those of the initial one-electron cleavage of the carbon–bromo bond. Step (*2*) is assumed to be very fast in these conditions since Hg is a good radical trap[1 – 6,12], and so free $Bu^{\bullet}$ is not present near to the Hg electrode to be directly reduced to Bu^{-}. On the other hand, $BuHg^{\bullet}$ must be a quite stable radical in the reaction layer provided that it is separately reduced in the second process of 1-bromo-2-butene following steps (*5*) – (*7*) in polarography (wave II) and CV (peak R_2). Peak O_2 found for this compound in CV using TEA^{+} as supporting cation (see Fig. 1*a*) is then associated to the oxidation of $BuHg^{-}$ to $BuHg^{\bullet}$. The fact that this peak was also observed in the presence of phenol excludes a noticeable protonation of $BuHg^{-}$ in the time scale of the experiment. The increase in height of peak R_2 of 1-bromo-2-butene with increasing v (se Fig. 2) can be explained if $BuHg^{\bullet}$ undergoes a slow chemical reaction on the stationary electrode surface, step (*3*), which is not observed in polarography because of the periodical renewing of the drop. Step (*3*) can then be envisaged as a surface reaction, as also proposed by other authors[4 – 6]. Since the resulting BuHgBu has little stability[3,6], it seems reasonable to consider its decomposition in step (*4*) to form diolefins. This is supported by the fact that no peak attributable to the irreversible reduction of BuHgBu to Bu^{-} has been observed in CV, in contrast to the peak found by Bard and Merz[4] for the electroreduction of 1-bromo-2-propene in acetonitrile.

In all media the irreversible one-electron charge transfer reaction (*1*) is the rate-determining step (rds) of the first one-electron reduction process of 1-bromo-2-butene in polarography and CV, and also of the overall two-electron process observed for 1-bromo-2-butene at the rotating Hg disk electrode. The rate determining step for the first-order EC mechanism taking place in the second reduction process of 1-bromo-2-butene (steps (*5*) – (*7*)) depends on the experimental conditions tested. In polarography, the rate determining step is decomposition of $BuHg^-$ to Bu^- in step (*6*). This is consistent with the relative stability of $BuHg^-$ near to the electrode surface since its oxidation by CV in peak O_2 is observed even at low scan rates (see Fig. 1*a*), whereas oxidation of Bu^-, which occurs in peak O_3 as will be discussed below, is not observed in the same conditions because of the higher rate of step (*7*). The quasi-reversible behaviour found for the O_2/R_2 couple of 1-bromo-2-butene in CV using TEA^+ can be ascribed to similar rates of steps (*5*) and (*6*), whereas the irreversibility observed for peak R_2 using TBA^+ indicates that reaction (*5*) is the rate determining step.

The single irreversible two-electron reduction process found in DMF for 1-chloro-2-butene on a Hg electrode and for both 1-halo-2-butenes on a gold electrode can be explained by the following general mechanism, also proposed[1] for the electroreduction of other organic halides:

$$BuX + e \longrightarrow Bu^{\bullet} + X^- \qquad (1')$$

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

$$Bu^- + H^+ \longrightarrow BuH \qquad (7)$$

$$\text{and/or} \qquad Bu^- + BuX \longrightarrow Bu\text{–}Bu + X^- , \qquad (8)$$

where the irreversible one-electron cleavage of the carbon bond of BuX is the rate-determining step. In this case, the initially electrogenerated allyl radical $Bu^{\bullet}$ is immediately reduced to Bu^- at the applied potential in step (*2'*) via a reversible one-electron transfer. The observed increase of I_l and I_p^c with the addition of phenol for the single reduction process of 1-chloro-2-butene (see Table I) can be explained[1 – 3] by nucleophilic attack of Bu^- on incoming BuCl to form Bu–Bu (step (*8*)), which causes a decrease in concentration of substrate available for reduction. Experimental results indicate that this reaction occurs unless excess phenol is added, so that practically all Bu^- becomes protonated. Step (*8*) is slower than step (*7*), where Bu^- is protonated to yield olefins, and occurs in some extent when reduction of 1-halo-2-butenes takes place in a single process. The formation of diolefins and butenes during the electrolysis of 1-chloro-2-butene can then be explained from competition between steps (*7*) and (*8*).

For 1-bromo-2-butene, however, CV results suggest that diolefins are also formed in electrolysis via coupling of $BuHg^{\bullet}$, following steps (*3*) and (*4*), as proposed by Kirrmann and Kleine-Peter[5,6].

The redox pair O/R found for 1-bromo-2-butene and 1-chloro-2-butene in CV on gold (see Fig. 3) can be associated to the $Bu^-/Bu^{\bullet}$ couple. The disappearance of this redox pair upon phenol addition can be explained[12] by fast protonation of Bu^- and for this reason, it is not present in the reaction layer when its oxidation potentials are reached on the anodic scan.

Taking into account that the set of secondary peaks of 1-halo-2-butenes in CV at Hg (see Fig. 2) appear at the same potential region as O/R couple at gold and that they also disappear upon phenol addition, it seems reasonable to consider that Bu^- is also the electroactive species in peaks O_3 of 1-bromo-2-butene and 1-chloro-2-butene at Hg. In each of these peaks, Bu^- is then oxidized to $Bu^{\bullet}$ and the slight difference between their anodic peak potentials (see Fig. 2) can be ascribed to different surface interactions between Hg and Bu^-, possibly involving the halide ions liberated in their primary reduction processes. Secondary reduction peaks R_3 and R_4 of both compounds showed similar peak potentials and can be associated[17] to reduction of $Bu^{\bullet}$ to Bu^- via an adsorption process (peak R_3) or a diffusion controlled reaction (peak R_4).

RRDE results for 1-halo-2-butenes in DMF are also consistent with the existence of basic intermediates in their reduction paths. Since the anodic wave of 1-bromo-2-butene at the rotating Hg ring electrode raises from a more negative disk potential than the half-wave potential of its disk cathodic wave (see Table III), $BuHg^-$ along with Bu^- coming from the second reduction process can be assumed to be the intermediates oxidized in the ring wave of this compound, in agreement with the higher stability of $BuHg^-$ found in CV, as stated above. The presence of an adsorption maximum in anodic currents of 1-bromo-2-butene at $\omega > 200$ r.p.m. (see Fig. 4) can then be explained by oxidation of $BuHg^-$ to $BuHg^{\bullet}$ on the ring electrode surface. The ring anodic current of 1-chloro-2-butene, however, appears at more negative disk potentials than that of 1-bromo-2-butene and does not show any adsorption maxima. In addition, its N_k values are three times lower than those determined for 1-bromo-2-butene (see Table III). All these findings suggest that the ring wave of 1-chloro-2-butene is mainly due to oxidation of Bu^- to $Bu^{\bullet}$.

In conclusion, reduction of allyl bromides in two consecutive one-electron processes in polarography can be explained by the low energy of the carbon–bromo bond and the high stability of the allylmercury radical in the medium, making it possible that this radical can be reduced to the allylmercury anion at more negative potentials than the one-electron cleavage of the carbon–bromo bond occurring in the first wave. For allyl chlorides, a single two-electron processes takes place because a much higher energy is required to break the carbon–chloro bond via a one-electron reduction step and then, potentials for this process are more negative than those needed for reduction of the intermediate allyl radical.

REFERENCES

1. Lund H., Baizer M. M. (Eds): *Organic Electrochemistry. An Introduction and a Guide*, 3rd ed., Chap. 8. Marcel Dekker, New York 1991.
2. Petrovich J. P., Baizer M. M.: Electrochim. Acta *12*, 1249 (1967).
3. Baizer M. M., Chruma J. L.: J. Org. Chem. *37*, 1951 (1972).
4. Bard A. J., Merz A.: J. Am. Chem. Soc. *101*, 2959 (1979).
5. Kirrmann A., Kleine-Peter M.: Bull. Soc. Chim. Fr. *1957*, 894.
6. Kleine-Peter M.: Bull. Soc. Chim. Fr. *1957*, 899.
7. Casado J., Doménech J., Galardo I.: Monatsh. Chem. *115*, 1143 (1984).
8. Ramaley L., Brubaker R., Enke C. G.: Anal. Chem. *35*, 1088 (1963).
9. Brillas E., Costa J. M.: J. Electroanal. Chem. *69*, 435 (1976).
10. Galus Z.: *Fundamentals of Electrochemical Analysis*, Chaps 7 and 9. Ellis Horwood, Chichester 1976.
11. Matsuda H., Ayabe Y.: Z. Elektrochem. *59*, 494 (1955).
12. Casado J., Ortega M., Gallardo I.: Collect. Czech. Chem. Commun. *54*, 911 (1989).
13. Pleskov Y. V., Filinovskii V. Y.: *The Rotating Disk Electrode*. Consultant Bureau, New York 1976.
14. Simonet J., Martinet P., Doupeux H., Bretelle D.: Bull. Soc. Chim. Fr. *1970*, 808.
15. Andrieux C., Gallardo I., Saveant J. M., Su K. B.: J. Am. Chem. Soc. *108*, 638 (1986).
16. Webb J. L., Mann C. K., Walborsky H. M.: J. Am. Chem. Soc. *92*, 2042 (1970).
17. Garrido J. A., Rodríguez R. M., Bastida R. M., Brillas E.: J. Electroanal. Chem. *324*, 19 (1992).