

Kinetics and mechanism of the reaction between 4-hexadecylbenzenediazonium ions and vitamin C in emulsions: further evidence of the formation of diazo ether intermediates in the course of the reaction

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The kinetics and mechanism of the reaction between hydrophobic 4-hexadecylbenzenediazonium ions, 16-ArN_2^+ and vitamin C, VC, in a model emulsion prepared by mixing octane, acidic (HCl) water and the non-ionic surfactant hexaethyleneglycol monododecyl ether, $C_{12}E_6$, were investigated. Because emulsions are opaque, linear sweep voltammetry, LSV, was employed to monitor the reaction. Voltammograms of 16-ArN_2^+ in emulsions show two reduction peaks as in aqueous systems. The half-life for the spontaneous decomposition of 16-ArN_2^+ in the emulsion was estimated as $t_{1/2} = 14.5$ h at $T = 25^\circ\text{C}$. Upon addition of VC to the system, the first reduction peak of 16-ArN_2^+ disappears almost immediately and a new reduction peak is detected at $E_p = -0.25$ V. Electrochemical titration of 16-ArN_2^+ shows that the new peak corresponds to the formation of a 1:1 adduct. The $i_p(E_p = -0.25$ V) values can be linearly correlated with $[16\text{-ArN}_2^+]$ and the observed rate constants, k_{obs} , were determined by fitting the (i_p, t) data to the integrated first order equation. The variation of k_{obs} with $[\text{VC}]$ follows a saturation kinetics profile, consistent with the formation of an intermediate in a pre-equilibrium step. All the evidence is consistent with a reaction mechanism comprising two competitive pathways, the spontaneous $\text{D}_N + \text{A}_N$ mechanism and the unimolecular decomposition of a transient diazo ether (DE) formed in a pre-equilibrium step. The data allowed estimations of the interfacial rate constant for the reaction between 16-ArN_2^+ and VC^- but did not allow the determination of the equilibrium constant for the DE formation. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: arenediazonium ions; emulsions; vitamin C; diazo ethers; O-coupling; kinetics

INTRODUCTION

Arenediazonium salts, $\text{ArN}_2^+ \text{X}^-$, constitute an important class of organic compounds because of the wide variety of chemical processes that they may undergo just by making slight changes in the reaction conditions.^[1–5] For instance, the reaction of 4-nitrobenzenediazonium ions in aqueous acid follows first-order kinetics with a half-life $t_{1/2} = 1383$ min at $T = 50^\circ\text{C}$, with 4-nitrophenol as the main dediazonation product, but when the reaction is carried out in a 10% MeOH/H₂O (v:v) mixture, non-first-order kinetics are obtained with $t_{1/2} \approx 6$ min and the main dediazonation products are 4-nitrobenzene and 4,4' dinitrobiphenyl, suggestive of a radical mechanism.^[6]

$\text{ArN}_2^+ \text{X}^-$ are mostly obtained by diazotization of primary amines with NO_2^+ donors.^[3,5,7] When the counterion X^- is a halide ion, special precautions must be taken when manipulating them because they are potentially dangerous; they may be extremely shock-sensitive, especially when completely dry and may detonate.^[7–9] This low stability of arenediazonium salts has been a limiting factor to quantitative investigations of their chemical properties, and the usual procedures involved the preparation of arenediazonium salts *in vitro* immediately prior to their use in a variety of chemical processes.^[7] The explosive character is diminished when prepared by employing high molecular weight

complex anions, for example, $\text{X}^- = \text{BF}_4^-$, leading to a significant improvement in their use and manipulation because they can be stored safely under proper conditions for a long time with negligible decomposition,^[10,11] and in fact some of them are commercially available. The synthesis of arenediazonium o-benzenedisulfonimides^[12] and arenediazonium trifluoroacetates^[13] has also been proposed because of their significant stability under proper storage conditions.

In addition to the well-recognized importance in synthetic and azo dye chemistry, their role in carcinogenic and mutagenic processes is being explored^[14–16] and new and interesting applications of arenediazonium salts are emerging. For instance, the oxidizing properties of ArN_2^+ ions have been exploited to modify carbon surfaces creating nanotubes, biosensors and coatings.^[17,18] Other current usages exploit the unique charac-

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teristics of the reaction between ArN_2^+ ions and weakly basic nucleophiles to probe interfacial compositions of colloidal aggregates.^[19]

We are currently determining the distribution of polar organic molecules in emulsified systems by using arenediazonium ions as chemical probes.^[20,21] Knowledge of antioxidant distribution in food emulsions is important because the efficiency of antioxidants in inhibiting lipid peroxidation depends, among others, on their distribution within the different regions of the system.^[21-23]

We are specially interested in natural antioxidants such as vitamin C, VC, because it is an essential micronutrient for man with many biological roles,^[24,25] showing a powerful antioxidant activity both directly via scavenging reactive oxygen species (ROS) and indirectly through regeneration of other antioxidant systems such as α -tocopherol (vitamin E).^[26-28]

Ascorbate ions (VC^-) have been used^[29,30] to promote diazoniazation of ArN_2^+ in the presence of intentionally added metal ions like Cu^{+2} , and Doyle *et al.*^[31] reported that VC reacts with $4-X-C_6H_4-N_2^+$ ($X = -NO_2$, $-Cl$ and $-NHC_6H_5$) to yield stable compounds whose structures have been spectroscopically identified as 3-O-arenediazoascorbic acids (diazo ethers). In contrast, Reszka and Chignell^[32] have recently found that reaction of $4-X-Ph-N_2^+$ ($X = -NO_2$, *p*-Cl, $-Br$, $-OMe$, $-N(Et)_2$) with H_2A under similar conditions ($pH = 7$) generate aryl radicals. In previous studies on natural food systems, we reported a novel method to determine VC in freshly prepared orange juice based on the accelerating effect of VC on the diazoniazation of 3-methylbenzenediazonium ions^[33] and in subsequent work we investigated the mechanism of the reaction in aqueous and micellar systems and modelled the observed pH dependence.^[34-37]

In the continuation of the preceding work, and to expand the current knowledge on the reactivity of ArN_2^+ ions with natural antioxidants, we have undertaken a kinetic study of the reaction between the hydrophobic 4-hexadecylbenzenediazonium ions, 16-ArN_2^+ and VC in an emulsified system prior to exploring their distribution in model food emulsions. The chemical structures of the emulsifier C_{12}E_6 , 16-ArN_2^+ and VC are given in Scheme 1.

Emulsions, or macroemulsions, represent a major group of colloidal systems which are present either as end-product or during the processing of products in a huge range of technological areas including the food, agrochemical, pharmaceutical, cosmetic, paint and oil industries, among others.^[38,39] Salad dressings, mayonnaise, milk, hand lotion and paints are all familiar examples of emulsions. Because of the size of the droplets, emulsions are opaque and thus common spectroscopic

techniques such as UV-VIS cannot be employed to monitor reactions and special protocols need to be developed. In the present work, we exploited the electrochemical characteristics of arenediazonium ions to investigate further their reactions in opaque systems by employing linear sweep voltammetry, LSV, which allows real-time monitoring of electroactive analytes. Previous electrochemical work provides a solid groundwork for the use of arenediazonium ions as electrochemical probes in a variety of systems.^[37,40-42]

In addition to the kinetics and mechanism of the reaction, the study may be pertinent to the food industry due to the extensive use of VC as a natural antioxidant and of some interest to biochemists. ArN_2^+ ions may behave as strong oxidizing agents undergoing homolytic fragmentation to produce aryl radicals upon reacting with relevant electron donors including antioxidants such as *tert*-butyl hydroquinone,^[43] and there is good evidence that the ability of arenediazonium ions to generate radicals may be responsible, to some extent, for the mutagenic and carcinogenic properties of aromatic diazonium compounds.^[32,44,45-49]

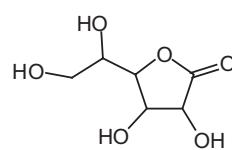
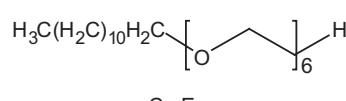
EXPERIMENTAL

Instrumentation

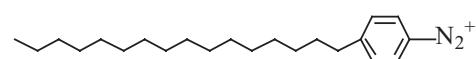
Voltammograms (LSV) were obtained on an Autolab Eco Chemie, model PGSTAT10, attached to a Metrohm model 663 Stand, and a computer for data manipulation and storage. The multimode-working electrode was used in the DME mode. The three-electrode system was completed by means of a glassy carbon rod (2 × 65 mm) auxiliary electrode and an Ag/AgCl (3 M KCl) reference electrode. All potentials given hereafter will be relative to above mentioned Ag/AgCl electrodes.

Materials

Octane, VC and the materials employed in the preparation of 4-hexadecylbenzenediazonium tetrafluoroborate were of the maximum purity available (Aldrich). The non-ionic surfactant hexaethylene glycol monododecyl ether, $C_{12}E_6$, density = 1 g/ml, was purchased from Fluka (98%). Diluted HCl solutions were prepared from concentrated HCl (Riedel de Häen) and its concentration was determined by means of potentiometric measurements. All solutions were prepared with Milli-Q grade water.



vitamin C



4-hexadecylbenzenediazonium, 16-ArN₂⁺

Scheme 1. Chemical structures of the non-ionic surfactant hexaethyleneglycol monododecyl ether, $C_{12}E_6$, the hydrophobic 4-hexadecylbenzenediazonium ion (synthesized as tetrafluoroborate) and vitamin C

4-Hexadecylbenzenediazonium tetrafluoroborate, 16-ArN_2^+ , was prepared from 4-hexadecylaniline (Sigma) following a standard non-aqueous procedure as described elsewhere.^[11] Stock $16\text{-ArN}_2^+ \text{BF}_4^-$ solutions were prepared in acetonitrile and kept in the dark at low temperature to minimize its decomposition.

Emulsion preparation

Emulsions of 1:1 and 2:3 octane-to-water volume ratio (10 ml) were prepared in a beaker by mixing together with a magnetic stirrer bar 5 ml of octane, 5 ml of aqueous 3 mM HCl and 4 ml of octane and 6 ml of aqueous 3 mM HCl, respectively, and a weighed amount of the emulsifier C_{12}E_6 . A single aqueous stock solution of 3 mM HCl (pH = 2.55), obtained by diluting concentrated reagent grade HCl, was used to prepare all the emulsions to keep aqueous phase acidity the same in all runs. Freshly prepared emulsions were transferred to the pre-thermostated (25 °C), covered, electrochemical cell. N_2 gas (99.999%) was used to purge the emulsion for at least 30 min while thermostating. Magnetic stirring was maintained during the purging and throughout the reaction to minimize phase separation and to ensure rapid mixing of all added reactants. No phase separation was observed for at least 3 h at room temperature.

Methods

Kinetic data were obtained by employing LSV. Voltammograms of 16-ArN_2^+ in emulsions of different oil-to-water ratios show two reduction peaks, in keeping with previous electrochemical results.^[33,37,40] The first one, Fig. 1A, appears at $E_p \sim -0.07$ V and is associated with the transfer of one electron. It was first proposed^[50–53] that the reduction of ArN_2^+ ions leads to the formation of the arenediazetyl radical, $\text{ArN}_2\cdot$, but recent work by Andrieux and Pinson^[54] showed that there are no diazetyl radicals involved in the reduction of ArN_2^+ in acetonitrile. The second reduction peak (not shown in Fig. 1A for the sake of clarity) appears at $E_p \sim -1.2$ V and is associated with a $3\text{e}^-/3\text{H}^+$ uptake to yield finally the corresponding arylhydrazine, ArNHNH_2 .^[53] The effects of experimental (concentration, temperature, pH, etc.) and instrumental (scan speed, initial potential, and so forth) parameters on the peak potential of the first reduction peak of 16-ArN_2^+ were investigated (data not shown) and small variations in the reduction peak potential of 16-ArN_2^+ , lower than 0.05 V, were detected. These small changes in the E_p values of a given analyte are commonly observed in electrochemical studies.^[40,55,56]

The reactions of 16-ArN_2^+ with VC in emulsions were carried out as follows. Once the freshly prepared emulsion was thermostated and degassed in the electrochemical cell, an aliquot (50–100 μl) of a recently prepared aqueous acid VC solution was incorporated into the emulsion and the mixture was degassed again for another 3 min. The reaction was initiated by adding an aliquot (10–50 μl) of a freshly prepared $16\text{-ArN}_2^+ \text{BF}_4^-$ solution and the reaction was monitored electrochemically by collecting voltammograms of the reaction mixture at convenient times. In all runs, the final VC concentration was at least 10 times higher than that of $16\text{-ArN}_2^+ \text{BF}_4^-$. The variations in the peak current (refer to Section 'Results') with time were obtained from the voltammograms and fitted to the integrated first order Eqn (1). Linear relationships were obtained for at least $3 t_{1/2}$ with typical correlation

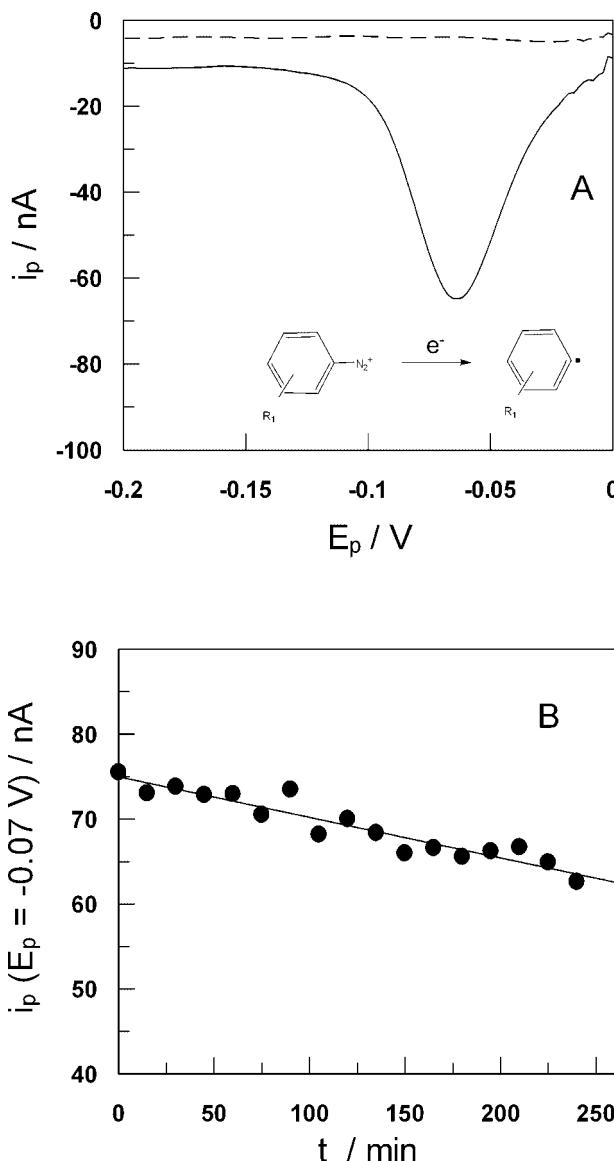


Figure 1. (A) Typical voltammogram (LSV) of 16-ArN_2^+ in a 1:1 (v:v) octane to water ($[\text{HCl}] = 3 \text{ mM}$) emulsion containing 0.05 g of C_{12}E_6 showing the first reduction peak. The dashed line is the voltammetric signal of the emulsion (background signal). (B) Variation of $i_p (E_p = -0.07 \text{ V})$ with time for the spontaneous decomposition of 16-ArN_2^+ in a 1:1 oil to water (v:v) emulsion. $T = 25 \text{ }^\circ\text{C}$, $E_i = 0.00 \text{ V}$; $\Delta E = -2 \text{ mV}$; $v = 0.5 \text{ V/s}$

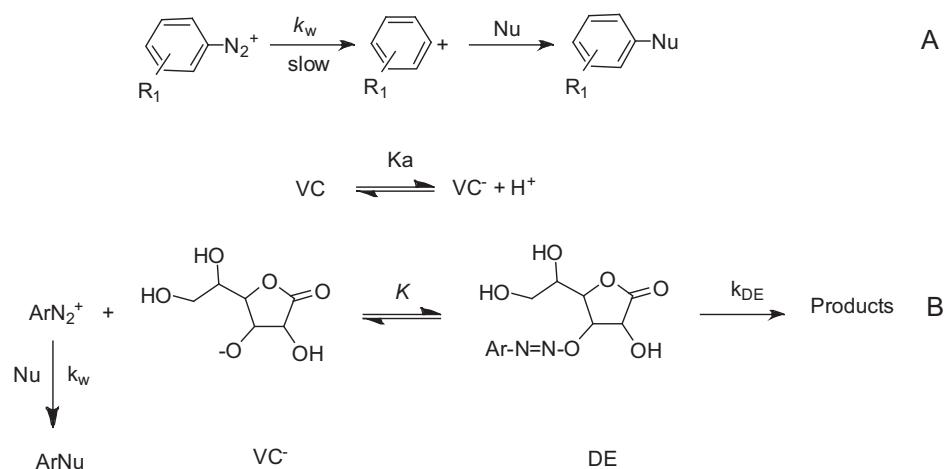
coefficients higher than 0.998. Duplicate or triplicate runs gave k_{obs} values with deviations lower than 7%.

$$\ln \frac{(i_p)_t - (i_p)_\infty}{(i_p)_0 - (i_p)_\infty} = -k_{\text{obs}} t \quad (1)$$

RESULTS

Stability of 16-ArN_2^+ in octane-water- C_{12}E_6 emulsions

Prior to studying the kinetics of the reaction with VC, the stability of 16-ArN_2^+ in 1:1 and 1:4 octane-to-water emulsions was checked



Scheme 2. (A) Basic representation of the $\text{D}_\text{N} + \text{A}_\text{N}$ dediazoniation mechanism. (B) Proposed mechanism for the reaction between arenediazonium ions and vitamin C comprising two competitive mechanisms, the $\text{D}_\text{N} + \text{A}_\text{N}$ pathway and the unimolecular decomposition of the transient diazo ether DE formed in a pre-equilibrium step. Refer to text for details

by monitoring the variation in the peak current of the first reduction peak with time. Figure 1B shows that, in a 1:1 emulsion, $i_p(E_p \sim -0.07 \text{ V})$ decreased by 17% within 4 h. Romsted and coworkers^[57,58] showed that 16-ArN_2^+ ions trap the $-\text{OH}$ groups of non-ionic surfactants via spontaneous decomposition of 16-ArN_2^+ , which generates, in the rate-determining step, an aryl cation that further reacts with the $-\text{OH}$ group yielding the corresponding alkyl aryl ether, that is, through the $\text{D}_\text{N} + \text{A}_\text{N}$ mechanism, Scheme 2A. Because octane does not react with ArN_2^+ ions and there are no potential reducing agents present in the emulsion, one can assume that the spontaneous decomposition of 16-ArN_2^+ in the emulsion takes place through the well-established $\text{D}_\text{N} + \text{A}_\text{N}$ mechanism, that is, rate-determining formation of a highly unstable aryl cation that further reacts with any nucleophile available in its solvation shell, Scheme 2A, and a value for the spontaneous decomposition of 16-ArN_2^+ in the emulsified system of $t_{1/2} \approx 14.5 \text{ h}$ can be estimated. Similar results were obtained when employing a 1:4 emulsion, suggesting that the oil-to-water ratio has little effect on k_{obs} for the spontaneous decomposition, in keeping with the extraordinary insensitivity of heterolytic dediazoniations to changes in solvent polarity.^[5]

Effects of added [VC] on the electrochemical behaviour of 16-ArN_2^+

Addition of ascorbic acid to the emulsion leads to the almost immediate disappearance of the peak at $E_p \sim -0.07 \text{ V}$ and the appearance of a new one, not previously detected, at $E_p = -0.25 \text{ V}$, Fig. 2. The results are consistent with previous electrochemical results in aqueous and micellar solutions, where the detection of a new reduction peak was unambiguously associated to the formation of a transient diazo ether (DE) such as that shown in Scheme 2B between ArN_2^+ and the monobasic form of VC.

Electrochemical titration of 16-ArN_2^+ , Fig. 3A shows that the peak current at $E_p = -0.07 \text{ V}$ decreases upon increasing [VC] with a concomitant increase in the peak current of the new reduction peak at $E_p = -0.25 \text{ V}$, so that when $[\text{VC}] = [16\text{-ArN}_2^+]$, the reduction peak of 16-ArN_2^+ is not detected and the current of the new reduction peak levels off. The data, therefore, are

suggestive of the formation of a 1:1 adduct between 16-ArN_2^+ and VC. The relationship between the current i_p of the reduction peak at $E_p = -0.25 \text{ V}$ and $[16\text{-ArN}_2^+]$ is linear (correlation coefficient > 0.997), Fig. 3B, and the reaction between 16-ArN_2^+ and VC was studied by monitoring the changes in its peak current with time, refer to Experimental section.

Effects of [VC] on k_{obs}

As shown in Figs 3 and 4, addition of VC leads to the almost immediate disappearance of the reduction peak of 16-ArN_2^+ at $E_p \sim -0.07 \text{ V}$ and the detection of a new voltammetric peak at $E_p \sim -0.25 \text{ V}$. Therefore, the reaction was monitored by measuring the variations of $i_p(E_p = -0.25 \text{ V})$ with time and the corresponding k_{obs} values were obtained by fitting the (i_p, t) pairs of data to Eqn (1). As the reaction proceeds, $i_p(E_p \sim -0.25 \text{ V})$ decreases with time and becomes constant when the reaction is

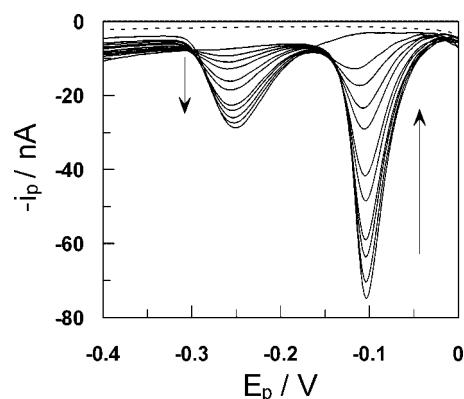


Figure 2. Effects of addition of increasing amounts of VC on the reduction peaks of 16-ArN_2^+ in a 2:3 octane/water ($[\text{HCl}] = 3 \text{ mM}$) containing $0.08 \text{ g C}_{12}\text{E}_6$ showing the disappearance of the reduction peak of 16-ArN_2^+ and the formation of a new one, not previously detected, at $E_p \sim -0.25 \text{ V}$, refer to text for further details. Voltammograms were obtained just after addition of VC. $T = 25^\circ\text{C}$, $[16\text{-ArN}_2^+] = 2.5 \times 10^{-4} \text{ M}$, $[\text{VC}] = 0\text{--}3.4 \times 10^{-4} \text{ M}$

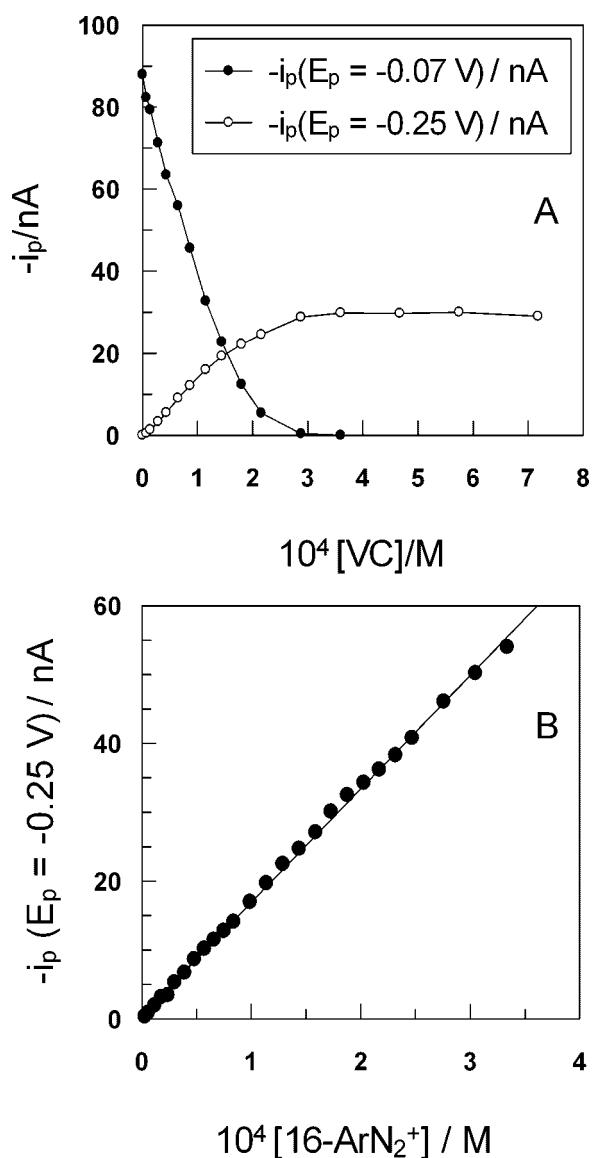


Figure 3. (A) Variation in the peak currents of the voltammograms obtained at constant $[16\text{-ArN}_2^+]$ upon increasing $[VC]$, refer to Fig. 2. Voltammograms were registered immediately after addition of the aliquots of VC . $T = 25^\circ\text{C}$, $[16\text{-ArN}_2^+] = 3.2 \times 10^{-4}$. 10^{-4} . (B) Calibration plot showing the linear relationship between $i_p (E_p = -0.25 \text{ V})$ and $[16\text{-ArN}_2^+]$. $T = 25^\circ\text{C}$, $[VC] = 1.05 \times 10^{-2} \text{ M}$

complete. Figure 4A shows a typical example of a kinetic run in a 2:3 emulsion.

The variation of k_{obs} with $[VC]$ follows a saturation kinetics profile, Figure 4B, consistent with a mechanism involving the formation of an intermediate that further decomposes in the rate-limiting step. For a given $[VC]$, k_{obs} values increase upon increasing pH by a factor of 3 on going from pH = 2.0 up to 2.5, suggesting that the reactive species is the ascorbate ion, in keeping with the results obtained in aqueous solution.

DISCUSSION

Electrochemical results in Figs 2 and 3, the saturation kinetics observed in Fig. 4 and the dependence of k_{obs} with the pH

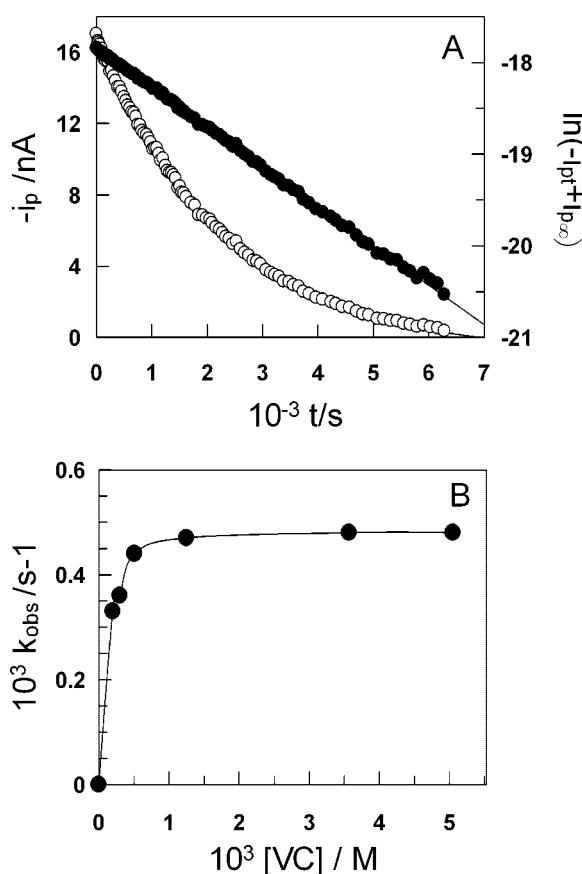


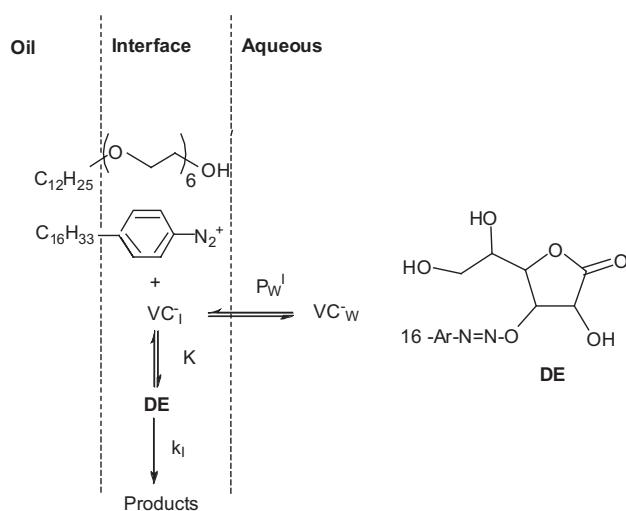
Figure 4. (A) Typical kinetic run obtained in a 2:3 octane to water ratio emulsion obtained by monitoring the disappearance of the reduction peak at $E_p = -0.25 \text{ V}$ (%) and linear plot (α) obtained by fitting the corresponding (i_p, t) data to the integrated first-order equation. (B) Variation in k_{obs} upon increasing $[VC]$. Emulsion composition: 4 ml octane, 6 ml water (HCl, pH = 2.0) and 0.066 g $C_{12}\text{E}_6$. $[16\text{-ArN}_2^+] \sim 2.6 \times 10^{-4} \text{ M}$, $T = 25^\circ\text{C}$

suggest that a mechanism similar to that proposed in aqueous acid and in micellar solutions is operating. These results can be interpreted in terms of the proposed mechanism indicated in Scheme 3.

Conceptually, emulsions can be divided in three different regions: the oil, aqueous and interfacial region where the emulsifier is located. Because 16-ArN_2^+ has a long hydrophobic chain ($C_{16}\text{H}_{33}$) and a cationic head group, it is insoluble both in water and oil,^[19–21] and the reactive diazonium group is located in the interfacial region. On the other hand, ascorbate ions should only partition between the water and interfacial regions. Therefore one would expect that negligible reaction occurs with VC in the oil and water regions, that is, the reaction takes place exclusively in the interfacial region. According to Scheme 3, the rate of the reaction is given by Eqn (2).

$$v = k_l(\text{DE}_l) = k_l K(16 - \text{ArN}_2^+)(\text{VC}_l^-) \quad (2)$$

where the subscript l denotes the interfacial region, k_l is the interfacial rate constant for the unimolecular decomposition of deformed adduct DE , and the parentheses () indicate concentration in moles per litre of the volume of a particular region. Concentrations in terms of the total volume of the emulsion, denoted in brackets [], can be obtained by multiplying the



Scheme 3. Proposed reaction mechanism between 16-ArN_2^+ and VC in emulsions

concentrations in moles per litre of a particular region by the volume of that region, that is, $[16\text{-ArN}_2^+]_T = (16\text{-ArN}_2^+) \phi_i$, where ϕ_i is the volume fraction of the interfacial region, which is equal to the volume of emulsifier employed divided by the total emulsion volume.^[21] By considering the corresponding mass balances and the ionization equilibrium of VC, the observed rate constant is given by Eqn (3)

$$k_{\text{obs}} = \frac{k_w + k_i B [VC_T]}{1 + B [VC_T]} \quad (3)$$

where k_w is the rate constant for the spontaneous decomposition of 16-ArN_2^+ in the interfacial region, k_i is the rate constant for the decomposition of the formed DE and B is a parameter that contains a combination of the equilibrium constant for the formation of the DE, K , the partition constant of VC, P_w^1 and the ionization constant, K_a , of VC and the acidity of the aqueous phase.

Because the thermal decomposition is negligible compared with the reaction through the complex, that is, $k_w \ll k_i B [VC_T]$, Eqn (3) can be rearranged to Eqn (4),

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_i} + \frac{1}{B K_i [VC_T]} \quad (4)$$

which predicts that a plot of $1/k_{\text{obs}}$ versus $1/[VC_T]$ should be linear. Figure 5 shows such linear dependence, from where one can obtain the values for the unimolecular decomposition of the DE, $k_i = (5 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ and $B = (10 \pm 1) \times 10^3$.

No direct comparison with reported rate constants for the unimolecular decomposition of the DE can be done because of the different experimental conditions employed; however, the obtained value is lower than those reported for the reaction between 3-methylbenzenediazonium ions and a number of 6-O-alkyl-L-ascorbic acid derivatives in aqueous and micellar systems.^[34–36]

As noted, the parameter B contains a combination of equilibrium constants, some of them currently unknown. Different methods to estimate partition constants in binary alcohol-water and oil-water systems are currently available,^[59,60] most of them based on the determination of the concentration of the analyte of interest in each region, but the physical impossibility of separating the interfacial region from the

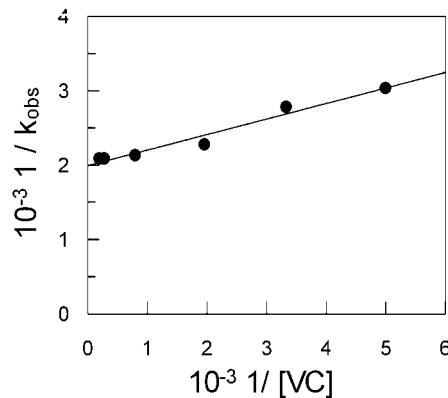


Figure 5. Double reciprocal plot according to Eqn (4) for the reaction between 16-ArN_2^+ and VC in an emulsion. Experimental conditions as in Fig. 4

aqueous or organic ones precludes their use, and new alternatives need to be considered.^[20,21] Therefore, the lack of reliable values for the partition constant P_w^1 of VC^- between the aqueous and interfacial region prevents estimations of the equilibrium constant for DE formation K .

DEs such as that shown in Scheme 3 are rarely formed as stable compounds,^[5] and as discussed elsewhere,^[36,37,61,62] it is believed that they are initially formed as the Z-DE isomer (kinetic control product) which further decomposes through two main pathways: an homolytic fragmentation pathway leading to reduction products (i.e. 16-ArH), and an isomerization pathway leading to the thermodynamically stable E-DE.

CONCLUSIONS

As final remarks, we would like to stress that we have been able to analyse the kinetics and the mechanism of the reaction between a hydrophobic arendiazonium ion, 16-ArN_2^+ , and VC in an opaque emulsified system. The results obtained are consistent with a mechanism comprising two competitive reaction pathways, the spontaneous $D_N + A_N$ mechanism and a rate-determining decomposition of a DE intermediate formed in a pre-equilibrium step. The DE was detected experimentally by electrochemical titration of 16-ArN_2^+ showing that a 1:1 adduct is formed. Evidence was also obtained from the analyses of the variation of k_{obs} with $[VC]$, which follows a saturation kinetics profile. Formation of intermediates of the DE type is not uncommon, and were experimentally detected in the course of reactions with different alcohols in aqueous, micellar and macromolecular solutions.^[6,34–37,42,62]

The results are in line with previous investigations concluding that the reaction mechanism in aqueous and in micellar systems is the same. Either addition of surfactants to the system or addition of hydrocarbon tails to the C_6 carbon atom of the ascorbic acid moiety does not change the mechanism of the reaction.^[35,36]

Our results are suggestive of VC^- ions partitioning into the interfacial region of the emulsions even though it is a very water-soluble antioxidant as shown by the rate enhancements obtained upon increasing $[VC]$. Different studies conclude that the activity of a given antioxidant in food systems depends not only on the environmental pH but also on a number of factors

including its partitioning between the different regions of the system, making such an evaluation of the antioxidant activity a difficult task.^[22,63,64] The results may be of some importance to the food and pharmaceutical industries. Oxidation of lipid-bearing foods such as vegetable oil, mayonnaise and spreads causes flavour deterioration. Oxidation of lipids not only produces rancid odours and flavours, but can decrease the nutritional quality and safety by the formation of secondary products in foods and by depleting the level of potentially beneficial polyunsaturated fatty acids.^[22,65,66]

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