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Microwave Activation of Electrochemical Processes: Enhanced Electrodehalogenation in Organic Solvent Media

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Abstract: The effect of high-intensity microwave radiation focused into a "hot spot" region in the vicinity of an electrode on electrochemical processes with and without coupled chemical reaction steps has been investigated in organic solvent media. First, the electrochemically reversible oxidation of ferrocene in acetonitrile and DMF is shown to be affected by microwave-induced thermal activation, resulting in increased currents and voltammetric wave shape effects. A FIDAP simulation investigation allows quantitative insight into the temperature distribution and concentration gradients at the electrode | solution interface. Next, the effect of intense microwave radiation on electroorganic reactions is considered for the case of ECE processes. Experimental data for the reduction of *p*-bromonitrobenzene, *o*-bromonitrobenzene, and *m*-iodonitrobenzene in DMF and acetonitrile are analyzed in terms of an electron transfer (E), followed by a chemical dehalogenation step (C), and finally followed by another electron-transfer step (E). The presence of the "hot spot" in the solution phase favors processes with high activation barriers.

1. Introduction

Several new methods for the activation of electrochemical processes have emerged in recent years, predominantly aiming at making processes more efficient, widening the range of applications, and introducing novel effects into electrochemical processes. Power ultrasound[1] and laser activation[2] have been demonstrated to allow in situ electrode cleaning without significant thermal effects. In contrast, predominantly thermal activation has been reported during direct heating of thin wires[3,4] or films,[5] radio frequency (rf) heating of the electrode in a channel flow cell,[6] laser pulse heating,[7] high frequency heating of microelectrodes,[8] and microwave activation.[9,10]

Thermal activation of electrochemical processes or "thermoelectrochemistry" has been proposed to be important in metallurgical research[11] and has played a key role in the development of electrochemical sensors.[12,13] The effects of elevated temperatures on electrochemical processes have been well-documented[14–17] but rarely fully explored, especially quantitatively. Recently, thermal effects on both diffusion processes and chemical reaction steps coupled to the interfacial electron transfer have been studied in a microelectrode flow system[18] and in a radio frequency heated channel cell.[19] Thermoelectrochemical experiments have been conducted by either heating all of the electrochemical cell (isothermal system) or, alternatively, only the working electrode compartment without a reference electrode (nonisothermal system). In the work reported below, effects of elevated temperatures induced by extreme microwave heating in a very small region (tens of microns) in the vicinity of the working electrode surface (nonisothermal) are discussed.

Only recently, has the activation of electrochemical processes by microwaves been introduced[9,20] as a new tool for both improving electrochemical processes and exploring microwave effects at electrified interfaces. Applications of microwave activation in voltammetric stripping analysis[21,22] have been

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(20) Marken, F.; Tsai, Y. C.; Saterlay, A. J.; Coles, B. A.; Tibbetts, D.; Holt, K.; Goeting, C. H.; Foord, J. S.; Compton, R. G. *J. Solid State Electrochem.* **2001**, *5*, 313.

proposed. Furthermore, the effect of focused microwave radiation on the formation of deposits at the electrode | solution interface has been discussed[23] in conjunction with a FIDAP simulation explaining the physical basis for thermal microwave effects.

In this report, the first quantitative account of the effect of high-intensity microwave radiation on electrochemical processes in nonaqueous media is presented. The oxidation of ferrocene (E process) is considered first as a model process before study of the chemically complex case of the electroreduction of some halogenated nitrobenzenes (ECE process). In the latter context we note the environmental interest in bringing about the effective dehalogenation and detoxification of haloaromatic molecules. A detailed physical picture of the effect of intense microwaves on mass transport and chemical processes at the electrode | solution interface is developed. FIDAP simulation methods are used for the quantitative interpretation of voltammetric data. It is demonstrated that effects of 2.45 GHz microwave radiation on electroorganic processes in microwave-absorbing (organic) media can be dramatic but are predominantly, possibly exclusively, thermal in nature.

2. Experimental Section

2.1. Reagents. Ferrocene, *p*-bromonitrobenzene, *o*-bromonitrobenzene, *m*-iodonitrobenzene, acetonitrile, and DMF (dimethylformamide) (all Aldrich) and NBu$_4$PF$_6$ (Fluka, electrochemical grade), have been obtained commercially and used without further purification. Solutions were deareated with argon (Pureshield, BOC) for at least 15 min prior to undertaking experiments.

2.2. Instrumentation. For electrochemical experiments a μ-Autolab II potentiostat system (Eco Chemie, The Netherlands) was used. The electrochemical cell (Figure 1a) consisted of a three-electrode arrangement with a Pt-mesh counter electrode, a saturated calomel electrode (SCE, Radiometer) as reference, and a special microwave working electrode with a 100 μm Pt disk sealed in glass (Micro Glass Instruments, Greensborough, Victoria 3088, Australia, or Scienglass, 46 Witney Road, Long Hanborough, Oxfordshire OX8 8BJ, U.K.). For microwave activation experiments a modified multimode microwave oven (Panasonic NN-3456, 2.45 GHz) with a modified power supply, a water energy sink, and a special port for the electrochemical cell was used. During experimentation a slow flow of electrolyte solution (ca. 10 μL s^{-1}) through the electrochemical cell was maintained to avoid overheating of the inlet and outlet solutions. Changing the anode current of the magnetron controlled the microwave intensity. *Before operation the system was tested for leaking microwave radiation with a radiation meter (Apollo XI microwave monitor, Apollo Ltd.).*

2.3. FIDAP Simulation Procedure. Numerical simulations were performed using the FIDAP version 8.52 finite element fluid dynamics program (www.Fluent.com) on a Silicon Graphics Origin 2000 running IRIX 6.4. FIDAP has been employed for solving electrochemical problems before[6,24] and is powerful in particular for complex systems with temperature gradients where diffusion coefficients and reaction rates vary with position. Simulations were carried out in two stages. The simulation for temperature and flow included the end of the microelectrode, represented as a cylinder of glass of diameter 0.2 cm and length 0.2 cm containing an axial 100 μm diameter platinum wire, and a cylindrical volume of solution of diameter 0.2 cm and length
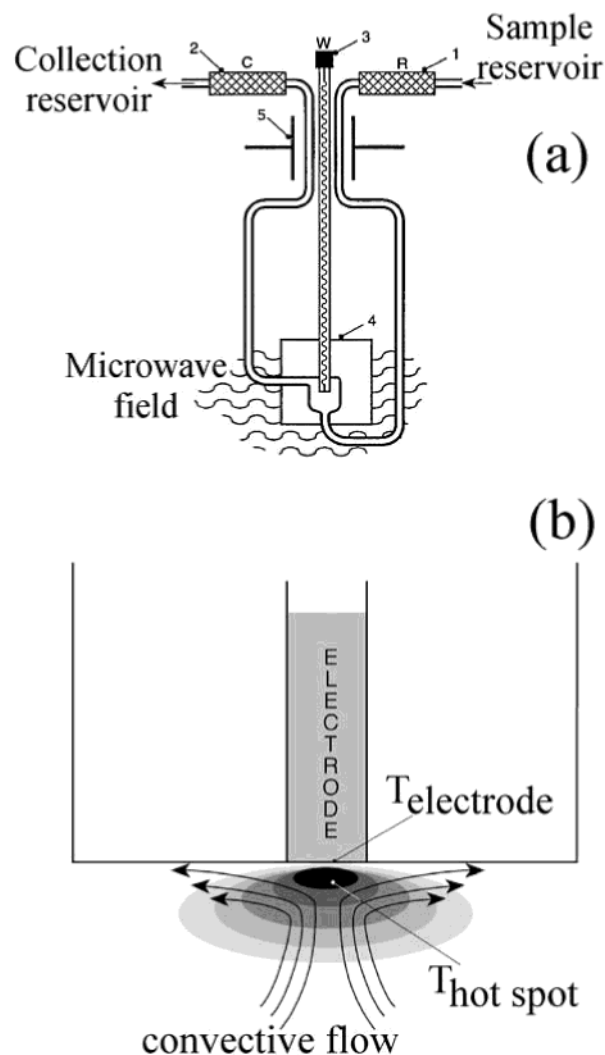

Figure 1. (a) Experimental cell for in situ microwave activation of electrochemical processes. Fresh electrolyte solution is pumped past the SCE reference electrode (1), through the port (5), into the sealed Teflon cell (4), and out past the Pt-gauze counter electrode (2). The working electrode (3) is located fixed in the center of the cell inside the multimode microwave cavity. (b) Pictorial presentation of the temperature distribution and convective flow pattern at the electrode surface in the presence of microwave radiation.

0.15 cm. A graded mesh was employed having a high density of elements close to the electrode face, with a lower density elsewhere to minimize computation requirements. Temperature-dependent solution properties (density, viscosity, thermal conductivity, volume expansion, dielectric constant) were compiled from data for acetonitrile in the DETHERM database (via CDS Daresbury;[25] see the Supporting Information). FIDAP includes a provision for Joule heating based on applied voltage and electrical conductivity but does not include provisions for high-frequency behavior. However, the voltage distribution at high frequency will be determined by the dielectric constants of the materials present and, therefore, electrical conductivities were assigned to reflect this (see the Supporting Information). The simulations (approximately 90 min of CPU time for each voltage) then yielded the temperature distribution and the convective flow velocities.

As chemical diffusion and reactions normally take place in a much smaller region close to the electrode, these simulations were carried out using a smaller model comprising solution only and with a finer mesh. This used a cylindrical volume of solution of diameter 200 μm

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and length 100 μm directly above the electrode, sufficient to enclose the diffusion layers. The values for temperature and flow velocity were transferred to this model by interpolation from the result databases of the temperature/flow runs and were held constant during diffusion and reaction simulations. This two-step approach reduces the computer resources required, and it is permissible since the reagent concentrations are too small to alter the physical properties of the solution. Diffusion and reaction simulations required approximately 5−10 min of CPU time and produced concentration distributions from which limiting currents were derived.

3. Results and Discussion

3.1. Microwave-Enhanced Electrochemical Processes: Reversible Electron Transfer in Organic Solvent Media. First, to establish the effect of microwave heating on a simple one-electron-transfer process in organic solvent media, the oxidation of ferrocene is investigated. The oxidation of ferrocene (eq 1)

$$Fc \rightarrow Fc^+ + e^- \tag{1}$$

is a highly reversible electrochemical process.[26] Voltammetric responses are therefore straightforwardly analyzed in terms of the formal standard potential, the limiting current, and the wave shape as a function of microwave power.

A set of voltammograms obtained at a range of different microwave powers for the oxidation of 2 mM ferrocene at a 100 μm diameter platinum-disk electrode immersed in acetonitrile is shown in Figure 2a. Sigmoidal steady-state responses are detected and, as expected, with increasing microwave power the limiting current increases. This effect has been qualitatively attributed[23] to the formation of a high-temperature region or "hot spot" in close proximity to the electrode surface. Focusing of microwaves at the end of the metal electrode is responsible for this highly localized thermal effect. Switching off the microwave power immediately results in return of the voltammetric characteristics to those observed at room temperature.[9] From this observation it can be inferred that (i) bulk heating effects remain insignificant and (ii) processes are detected under high-intensity microwave conditions.

The analysis of voltammetric data obtained in the presence of microwave radiation may be based on conventional procedures commonly applied in isothermal steady-state voltammetry.[27] In Table 1 data obtained for the oxidation of 2 mM ferrocene in acetonitrile are summarized. The half-wave potentials of the voltammetric traces show a characteristic trend toward higher potentials at elevated temperature. This shift is reflecting the electrode half-reaction entropy.[28] Therefore, the temperature at the electrode surface is known[19] to follow approximately a linear relationship: $dE^{o\prime}/dT = 0.53$ mV K^{-1}. This relationship allows the (average) temperature at the electrode surface (see Table 1, column 3) to be evaluated independently, without significant effects from other experimental parameters such as convection or thermal gradients. Also the shape and in particular the Tomeš criterion (the potential difference between the points where 75% of the limiting current is reached, $E_{3/4}$, and where 25% of the limiting current is reached, $E_{1/4}$) are sensitive to the temperature at the electrode
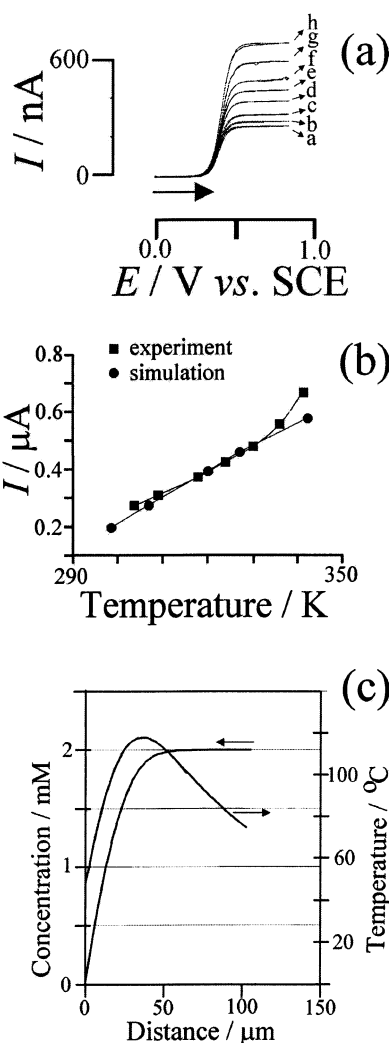

Figure 2. (a) Cyclic voltammograms (scan rate 0.1 V s^{-1}) for the oxidation of 2 mM ferrocene at a 100 μm diameter Pt-disk electrode immersed in acetonitrile (0.1 M NBu$_4$PF$_6$). Individual traces show different microwave intensities (a−h; see Table 1). (b) Plot of the experimentally observed (square) and simulated (circles) limiting currents against electrode surface temperature, $T_{electrode}$. (c) Plot (based on FIDAP simulation results) of the ferrocene concentration (left axis) and the temperature (right axis) versus the distance from the electrode surface.

surface. Both the experimental Tomeš criterion and the temperature at the electrode surface evaluated on the basis of[29] $E_{3/4} - E_{1/4} = 2.22RT/F$ are given in Table 1. Both procedures for the evaluation of the (average) electrode surface temperature can be seen to give consistent and reliable results.

A simulation approach based on FIDAP software has been employed recently[23] to provide insight into the complex combination of thermal and convection effects at the electrode surface. This approach is employed here for the case of ferrocene oxidation in acetonitrile. Parameters and data employed for the FIDAP simulation are summarized in the Supporting Information. The temperature-related density and viscosity changes are accounted for, and convection from the high-temperature region toward the electrode surface is observed. In fact, the effect of enhanced convection has recently been shown to be responsible for approximately half of the observed mass transport enhance-

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Table 1. Voltammetric Data (−1.8 to +1.0 V vs SCE Potential Window, Scan Rate 0.1 V $^{-1}$) for the Oxidation of 2 mM Ferrocene (Employed as Internal Temperature Reference) and for the Reduction of 2 mM m-Iodonitrobenzene in Acetonitrile (0.1 M NBu$_4$PF$_6$) at a 100 μm Diameter Platinum Electrode in the Presence of Microwave Radiation

| | ferrocene $E_{1/2}$/V vs SCE | $T_{electrode}$[b]/ K | Tomeš criterion/ mV | $T_{electrode}$[c]/ K | $|I_{lim}|/\mu$A | | |
entry					ferrocene	m-iodo-nitrobenzene	n_{eff}[d]
a	0.373	298	56.5	298	0.251	0.253	1.00
b	0.376	304	57.4	303	0.276	0.279	1.01
c	0.379	309	58.7	310	0.310	0.317	1.02
d	0.384	319	60.0	317	0.374	0.405	1.08
e	0.387	324	61.8	326	0.428	0.493	1.15
f	0.390	330	63.1	333	0.480	0.589	1.23
g	0.393	336	63.2	337	0.560	0.768	1.37
h	0.396	341	65.4	345	0.670	1.020	1.52

[a] Half-wave potential. [b] Calculated from half-wave potential assuming that $dE^{o\prime}/dT = 0.53$ mV/K.[19] [c] Calculated from the Tomeš criterion $E_{3/4} - E_{1/4} = 2.22RT/nF$[29] with $n = 1.0$. [d] Calculated on the basis of eq 3.

ment under microwave irradiation.[23] Changes in the diffusion coefficient constitute the other half. Simulation results are shown in Figure 2b. The plot shows mass transport controlled limiting currents as a function of electrode surface temperature ($T_{electrode}$). Deviations between simulation and experiment are observed at low temperature, where convection or non-steady-state effects may cause an apparent increase in the experimental current, and at high temperature, where bulk heating of the cell content during the course of the voltammetric experiment becomes significant.

The distribution of temperature and ferrocene concentration in the solution phase determined from the FIDAP simulation is shown in Figure 2c. It can be seen that the diffusion layer extends approximately 50 μm into the solution phase. The diffusion layer thickness parameter, which under constant-temperature conditions is easily estimated from the limiting current,[30] is affected by the temperature gradient at the electrode surface. The temperature can be seen to increase away from the electrode surface with a "hot spot" region at approximately 40 μm distance. The "hot spot" temperature, 118 °C, is considerably higher than the electrode temperature, 47 °C, and also much higher than the boiling point for acetonitrile, 81.6 °C. Under these conditions, the velocity of acetonitrile convection through the "hot spot" region is 0.1 cm s^{-1}, and therefore, the solvent passes through the high-temperature region in typically less than 100 ms. This short temperature transient is probably responsible for the avoidance of nucleation or onset of boiling. The parameter which governs the "hot spot" temperature is the thermal conductivity of the solvent, and for acetonitrile the thermal conductivity is low and effects are therefore more dramatic compared to, for example, water.

Very similar results were obtained for the oxidation of 2 mM ferrocene in DMF (0.1 M NBu$_4$PF$_6$) at a 100 μm diameter platinum-disk electrode. The microwave radiation causes considerable current enhancements. Table 2 summarizes voltammetric data obtained in DMF.

Next, it is interesting to ask how the "hot spot" induced by microwave radiation affects chemical processes coupled to the interfacial electron transfer. A reaction for cathodic dehalogenation processes following an ECE-type reaction sequence is investigated.
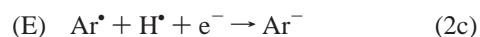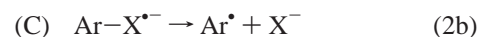
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Table 2. Voltammetric Data (−1.8 to +1.0 V vs SCE Potential Window, Scan Rate 0.1 V s^{-1}) for the Oxidation of 2 mM Ferrocene (Employed as Internal Temperature Reference) and for the Reduction of 2 mM p- or o-Bromonitrobenzene in DMF (0.1 M NBu$_4$PF$_6$) at a 100 μm Diameter Platinum Electrode in the Presence of Microwave Radiation

| ferrocene $E_{1/2}$/V vs SCE | Tomeš criterion/ mV | $T_{electrode}$[b]/ K | $|I_{lim}|/\mu$A | | n_{eff}[b] |
			ferrocene	p-bromo-nitrobenzene	
0.496	58	306	0.151	0.161	1.07
0.504	61	322	0.202	0.216	1.07
0.520	65	343	0.430	0.509	1.18
0.535	70	370	0.720	0.889	1.22

| ferrocene $E_{1/2}$/V vs SCE | Tomeš criterion/ mV | $T_{electrode}$[b]/ K | $|I_{lim}|/\mu$A | | n_{eff}[c] |
			ferrocene	o-bromo-nitrobenzene	
0.496	57	301	0.140	0.270	1.93
0.503	59	311	0.186	0.378	2.03
0.517	65	343	0.351	0.706	2.01
0.526	70	370	0.508	1.036	2.04

[a] Half-wave potential. [b] Calculated from data for the oxidation of ferrocene from the Tomeš criterion $E_{3/4} - E_{1/4} = 2.22RT/nF$[29] with $n = 1.0$. [c] Calculated on the basis of eq 3.

3.2. Microwave-Enhanced Electrochemical Processes: ECE Type Reactions in Organic Solvent Media. In Figure 3a a typical set of cyclic voltammograms obtained for the reduction of m-iodonitrobenzene at a 100 μm diameter platinum electrode immersed in acetonitrile and in the presence of microwave radiation is shown. The reduction process is accompanied by the rate-determining formation of free halide anions, I$^-$, and an aromatic radical, which undergoes further chemical and electrochemical reaction steps (eq 2).

$$\text{(E)} \quad \text{Ar–X} + \text{e}^- \rightarrow \text{Ar–X}^{\bullet-} \qquad (2a)$$

$$\text{(C)} \quad \text{Ar–X}^{\bullet-} \rightarrow \text{Ar}^\bullet + \text{X}^- \qquad (2b)$$

$$\text{(E)} \quad \text{Ar}^\bullet + \text{H}^\bullet + \text{e}^- \rightarrow \text{Ar}^- \qquad (2c)$$

In eq 2 Ar = nitrophenyl and X = I, Br. Experiments were conducted with p-bromonitrobenzene in DMF, with o-bromonitrobenzene in DMF, and with m-iodonitrobenzene in acetonitrile.

Experiments were always conducted with ferrocene acting as internal temperature reference. Comparison of the mass-transport-controlled limiting currents in steady-state voltammograms for the oxidation of ferrocene and for the reduction of halonitrobenzenes immediately allows the number of electrons transferred per molecule of nitrobenzene to be evaluated. With the diffusion coefficient for the compounds known, the effective number of electrons transferred per molecule of nitrobenzene diffusing to the electrode surface is approximately given by eq 3. In this equation I_{lim} is the experimental limiting current, D is

$$n_{eff} = \frac{n_{nitrobenzene}}{n_{ferrocene}} = \left| \frac{I_{lim,nitrobenzene}}{I_{lim,ferrocene}} \right| \frac{D_{ferrocene}{}^x c_{ferrocene}}{D_{nitrobenzene}{}^x c_{nitrobenzene}} \qquad (3)$$

the diffusion coefficient, x is a mass transport dependent exponent assumed here to be unity, and c is the concentration in bulk solution. This expression may fail if the temperature dependence of the individual diffusion coefficients, $D_{nitrobenzene}$ and $D_{ferrocene}$, are very different.[19] However, for voltammetric data discussed here this equation holds approximately. The number of effectively transferred electrons, n_{eff}, for the reduction

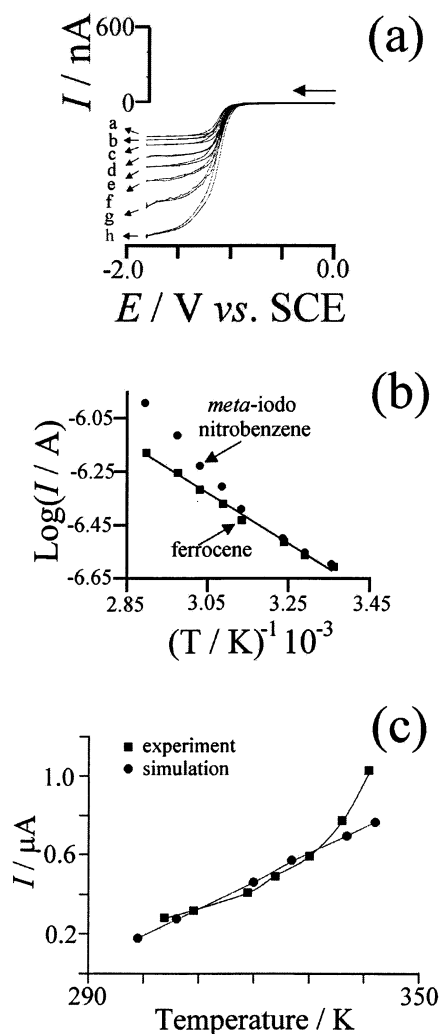**Figure 3.** (a) Cyclic voltammograms (scan rate 0.1 V s^{-1}) for the reduction of 2 mM *m*-iodonitrobenzene (in the presence of 2 mM ferrocene) at a 100 μm diameter Pt-disk electrode immersed in acetonitrile (0.1 M NBu$_4$PF$_6$). Individual traces show different microwave intensities (a−h; see Table 1). (b) Arrhenius type plot of the experimentally observed limiting currents for ferrocene oxidation and for *m*-iodonitrobenzene reduction. (c) Plot of the experimentally observed (square) and simulated (circles) limiting currents against electrode surface temperature, $T_{electrode}$.

of *p*-bromonitrobenzene remains approximately 1.0 for a temperature range $T_{electrode}$ = 300−370 K (see Table 2). Only at very high microwave intensity is a deviation detected. In contrast, the reduction of *o*-bromonitrobenzene in DMF gives approximately n_{eff} = 2.0 (see Table 2) for measurements in the same temperature range. These results suggest that *p*-bromonitrobenzene is reduced to the radical anion (eq 2a) with a follow-up chemical reaction step too slow to be detected within the time scale of the voltammetric experiments. Even at elevated temperature in the presence of microwave radiation the process is not detected. For the reduction of *o*-bromonitrobenzene the transfer of two electrons is always detected and, therefore, the chemical step in the ECE sequence outruns mass transport at all temperatures. The room-temperature rate constant k_{298} = 250 s^{-1} has been reported in the literature.[31]

An interesting intermediate case is observed for the reduction of *m*-iodonitrobenzene. Here, n_{eff} increases from 1.0 at low temperature to >1.5 at 345 K (see Table 1). When n_{eff} lies between 1.0 and 2.0, the rate constant for the chemical reaction step (eq 2b) becomes accessible. In conventional steady-state voltammetry a simple formula based on the comparison of the diffusion layer with the reaction layer has been employed for the determination of chemical rate constants.[30] However, thermal gradients in the vicinity of the electrode surface have effects which depend on the activation energy of a process. Therefore, the use of the simple formula becomes unwarranted and a full simulation has to be implemented for data analysis.

The plot in Figure 3c shows the experimentally observed limiting currents for the reduction of 2 mM *m*-iodonitrobenzene in acetonitrile together with limiting current data extracted from the FIDAP simulation. Agreement over a wide range of temperatures can be observed, and only at very high microwave intensity is a deviation detected (compare with data for the pure diffusion case in Figure 2c). The simulation was based on the temperature-dependent rate constant data, k_{298} = 0.30 s^{-1}, and the activation energy, E_a = 80 kJ mol^{-1}, reported recently.[19] The agreement between experiment and simulation suggests that within experimental error a purely thermal effect is detected in the presence of high-intensity microwave radiation.

4. Conclusions

It has been shown that microwave activation of electroorganic processes at small electrodes allows both mass transport and chemical processes coupled to the interfacial electron transfer to be enhanced. The effect observed here (in a microwave-absorbing solvent system) is thermal and is based on the formation of a "hot spot" region in the vicinity of the electrode surface. Temperatures in the "hot spot" region are considerably higher than those at the electrode surface and may considerably exceed the boiling point of the liquid. The thermal gradient at the electrode | solution interface affects processes according to their activation energy. Therefore, chemical steps are affected more strongly than mass-transport processes. In the future, it will be interesting to explore (i) the CE-type mechanism, in which chemical reaction intermediates are formed in the "hot spot" region and then transported toward the electrode, and (ii) processes in microwave-transparent solvent media.

Supporting Information Available: Details of the FIDAP simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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