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Radical Clocks, Solvated Electrons, and Magnesium. Heterogeneous versus Homogeneous Electron Transfer. Selectivity at Interfaces

Hassan Hazimeh,^{†,‡} Frédéric Kanoufi,^{*,‡} Catherine Combellas,[‡] Jean-Marc Mattalia,^{*,†} Caroline Marchi-Delapierre,[†] and Michel Chanon[†]

Laboratoire AM3, Case 561, UMR CNRS 6178, Faculté des Sciences et Techniques de Saint-Jérôme, Université Paul Cézanne (Aix-Marseille III), 13397 Marseille Cedex 20, France, and Laboratoire Environnement et Chimie Analytique, UMR CNRS 7121, ESPCI, 10 Rue Vauquelin, 75231 Paris Cedex 05, France

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Ammonia solutions of solvated electrons may be prepared by electrolyzing the solvent in the presence of $\text{Mg}(\text{BF}_4)_2$ and Mg^{++} provided by a magnesium anode. The reactions of these solutions ($-40\text{ }^\circ\text{C}$) with the two radical clocks 1-bromo-2-(3-butenyl)benzene **1** and 1-(allyloxy)-2-bromobenzene **7** (0.007–0.008 M) are examined. Both probes yield very high percentages of cyclized products ($>97\%$) when the concentration of solvated electrons is low (0.028 M). These percentages diminish when the metallic character of the solution is increased (0.183 M concentration in solvated electrons). These results strongly contrast with those obtained for the reactions of these radical probes with magnesium turnings or potassium lumps in THF. Under these conditions, the percentages of cyclized products are lower than 4%. We propose that the main cause of this contrasting behavior is the higher reducing efficiency of the heterogeneous electron transfer with respect to the homogeneous electron transfer. This holds even if the reducing agent in the bulk is one of the strongest known reducing agents (solvated electron). The causes for the striking difference between heterogeneous and homogeneous electron transfer are discussed in terms of selectivity within a double-layer perspective. These differences allow the rationalization of an apparent discordance. The behavior of MgX_2 (X = halogen) under pulse radiolysis conditions (Mostafavi's group) shows that MgX_2 are so weakly oxidizing that in most solvents they do not react with the solvated electron. Nevertheless, the reduction of MgX_2 by alkali metals (Rieke's method) is the basis for the preparation of very active slurries of magnesium. This principle has been widely extended for the preparation of various metallic nanoparticles. The difference between homogeneous and heterogeneous electron transfer to MgX_2 lies at the heart of the problem as explained in the framework of molecular electrochemistry at the cathode surface. Kinetic treatment of the selectivity at the metal–liquid interface is contrasted with selectivity obtained in homogeneous solution.

1. Introduction

Radical clocks have played an important role in disentangling the mechanistic subtleties of classical organic chemistry,^{1–7} organometallic chemistry,^{8–10} photochemistry,^{11–15} and bioorganic and bioinorganic chemistries.^{16–22} These molecular tools, which make it possible to monitor, at a microscopic level, which elementary steps occur in an overall transformation, have been far less used to gain insight into the events occurring at the solid–liquid interface involved in electrochemically induced reactions.²³ Hoffmann recently discussed the relative overlook of this tool to study reactions at the solid–liquid interface.²⁴ A good number of electrochemically induced radical cyclizations have been reported.^{25–35} For most of these examples, the purpose was not to use the tool “radical clock” to gain insight into the molecular events occurring in the close vicinity of the electrode surface. Some examples in this report illustrate that this direction of research could be fruitful: electrochemistry is an evergreen for the creation of radicals under a variety of controlled

conditions; radical clocks with structural variations tuned to answer selected questions may behave as actual spies either of the changing media or of the occurring rapid elementary reactions.

During studies on the mechanism of formation of aryl Grignard reagents, we obtained puzzling results, independently confirmed by Garst's team.^{36,37} When 1-bromo-2-(3-butenyl)benzene **1** was reacted with magnesium in THF, only very small amounts of cyclized products were obtained, the dominant product being the linear one. These results strongly differed from those reported by Beckwith and Bunnett when they had opposed the same radical clock to alkali metals in ammonia.³⁸ It was not easy to render our results comparable with these ones because magnesium is far less soluble in ammonia than alkali metals.^{39–41} Fortunately, Combellas's group reported an original electrochemical way to dissolve magnesium in liquid ammonia.^{42,43} We started a joint venture to study the reactivity of selected radical clocks toward such ammoniacal solutions.

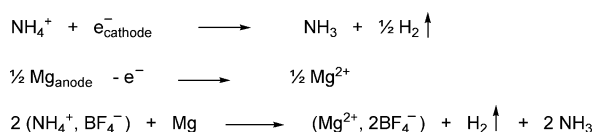
Alternatively, Mostafavi's group reported a series of experiments contrasting with Rieke's method for obtaining very reactive slurries of various metals. Mostafavi's group observed that MgX_2 salts (X = halogen) do not react with one of the strongest known reducing agents: the solvated electron.^{44,45} With

* Corresponding authors. Jean-Marc Mattalia e-mail: jean-marc.mattalia@univ-cezanne.fr; phone: +33 (0)4 91 28 27 78; fax: +33 (0)4 91 28 82 34. Frédéric Kanoufi e-mail: frederic.kanoufi@espci.fr.

[†] Laboratoire AM3.

[‡] Laboratoire Environnement et Chimie Analytique.

SCHEME 1



$\text{X} = \text{ClO}_4^-$, however, the reaction with the solvated electron in selected solvents (THF, diethyl ether, ethylenediamine) occurred. Even in this situation, the spectroscopic properties displayed by the created transients were in better agreement with an $(\text{Mg}^{++}, \text{electron pair})$ than with actual Mg^+ species.⁴⁶ In contrast with these results, Rieke prepared very active slurries of zerovalent magnesium by the reduction of MgX_2 with alkali metals in THF or other solvents.^{47–54} Reduction of metal salts provides the basic principle of one of the most used methods for preparing metallic nanoparticles whose importance keeps growing in several parts of chemistry.^{55,56} What could be the cause of these contrasting behaviors of MgX_2 ? Which factors rule the selectivity in the vicinity of a metallic surface?

2. Experimental Section

2.1. Starting Materials, Apparatus, and Instruments.

1-bromo-2-(3-butenyl)benzene **1** was prepared from the reaction of allylmagnesium bromide with 2-bromobenzyl bromide.^{37,38} 1-(Allyloxy)-2-bromobenzene **7** was prepared from the reaction of 2-bromophenol with allyl bromide in acetone/ K_2CO_3 .⁵⁷ Authentic samples of 3-butenylbenzene **2**,³⁷ 1-methylindane **4**,^{37,58} 1,2-bis(1-indanyl)ethane **6** (mixture of diastereomers),³⁸ and 3-methyl-2,3-dihydro-1-benzofuran **9**⁵⁹ were prepared as described in the literature. Phenol **8** was commercially available. Anhydrous NH_3 and NH_4BF_4 97% were, respectively, purchased from Air Liquide and Aldrich.

All electrochemical experiments were run in an undivided electrochemical cell whose temperature was maintained at -40°C with an ethanol bath cooled by a cryocooler (Neslab Cryocool). Before each experiment, the cell and electrodes were dried in an oven (100°C). All of the experiments were performed under an argon atmosphere (Arcal 1, argon U, Air Liquide).

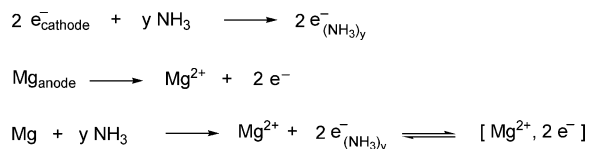
Electrolyses were performed under conditions of controlled current using a stainless-steel cathode (6 or 4 cm^2) and a magnesium anode (15 cm length \times 1 cm diameter). The controlled current was supplied with a stabilized power supply apparatus (DC Power Supply). The quantity of charge consumed was measured with an integrator Tacussel IG 5-N.

GC-MS analyses (electronic impact) were carried out at 70 eV. The procedure employed a He pressure of 0.4–0.8 bar and a temperature program from 80 to 280°C (held for 2.5 min) at $23^\circ\text{C}/\text{min}$. The injector was maintained at 270°C . Relative response factors were estimated from solutions of authentic samples.

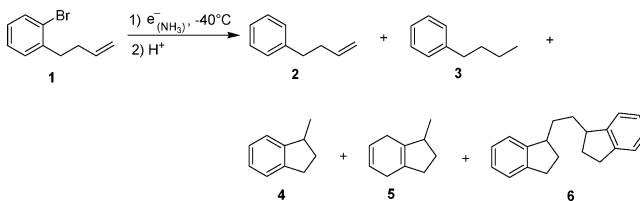
2.2. General Procedure. Preparation of the Supporting Electrolyte. The preparation of the supporting electrolyte is described in the Supporting Information. Its principle is shown in Scheme 1.

Reaction between Solvated Electrons and Radical Clocks. The second phase started when the blue color obtained during the first phase had faded away (the small excess of solvated electrons slowly reacts with traces of water or NH_3 to give H_2 and NH_2^-). The electrolysis was started again at a constant current of 0.1–0.4 A (for the solutions with low solvated electron concentration) or 0.5–1 A (for the most concentrated solutions) until the desired concentration of solvated electrons was obtained. The charge consumed was 150–180 C for the

SCHEME 2



SCHEME 3



less-concentrated solutions and 4000–4500 or 5700–6100 C for the solutions with high concentrations of solvated electrons. At this point, we obtained a NH_3 solution of $\text{Mg}(\text{BF}_4)_2$, plus solvated electrons whose charge is neutralized by the Mg^{++} cations formed at the anode (see the first paragraph of “Results and Discussion” for a more precise description). The electrodes were removed; the radical clock (**1** or **7**) was added to this solution up to a concentration of 0.007–0.008 M with a microsyringe, and the cell was closed with the stopper. After washing and drying, weighting the magnesium anode at the end of the reaction shows a loss of weight and indicates the quantity of solvated electrons, taking into account the quantity of magnesium consumed for the reduction of NH_4BF_4 . When one equivalent of magnesium is consumed, two equivalents of solvated electrons are formed (Scheme 2). In some experiments, the magnesium anode was weighted after the preparation of $\text{Mg}(\text{BF}_4)_2$ and at the end of the reaction; thus, the quantity of solvated electrons was directly available from the amount of magnesium loss.

At the end of reaction of **1** or **7**, solid NH_4BF_4 was added to acidify the solution until the disappearance of the blue color. Then the solution was poured in 40 mL of THF. When NH_3 had evaporated, the solution was analyzed by GC-MS.

Reaction between Radical Clock **1 and Solvated Electrons Progressively Created at the Cathode.** The supporting electrolyte was prepared from NH_4BF_4 (0.18 M) in liquid ammonia (62 mL) and *t*-BuOH (2.5 mL), as described in the Supporting Information. When the solution displayed the characteristic blue color of solvated electrons, the electrolysis was then continued for 40 C to ensure the complete reduction of NH_4^+ . The electrodes were removed, washed, and dried. When the blue color had faded away, 1-bromo-2-(3-butenyl)benzene **1** (0.008 M) was added and the electrodes were placed again in the cell. The solution was electrolyzed at low current (30–65 mA) until the total reduction of **1** and emergence of the blue color. Aliquots were removed, and the reaction was monitored by GC-MS. Under these conditions of electrolysis, the concentration of the solvated electrons increased linearly with the charge passed through the circuit because the electric yield was nearly quantitative. The concentration of the solvated electrons was estimated from the relation $q = nF$ ($F = 96500$ C). At the end of the reaction, solid NH_4BF_4 was added to acidify the solution until the disappearance of the blue color. Then the solution was poured in 40 mL of THF. When NH_3 had evaporated, the solution was analyzed by GC-MS. The reaction of **1** with the solvated electrons led to products **2–6** (Scheme 3). Products **2**, **4**, and **6** were identified by GC-MS analysis by comparison with authentic samples (see the Supporting Information).

TABLE 1: Reaction of Radical Clock 1 with Solvated Electrons (e^-) in Liquid Ammonia at $-40\text{ }^\circ\text{C}$ ($[1] = 0.007\text{--}0.008\text{ M}$, $[\text{Mg}(\text{BF}_4)_2] = 0.08\text{--}0.1\text{ M}$)^a

entry	q (C) ^b	$[e^-]$ M ^c	$e^-/1$ ^c	$t\text{-BuOH}/1$ ^d	time (min)	conv. ^e (%)	relative yields (%) ^e					cycl. (%) ^f
							2	3	4	5	6	
1	160	0.028	3.76		14	100	2	0	87	0	11	98
2	150	<0.04 ^g	<5.3 ^g	55 ^h	7	80	1	0	85	1	13	99
3	4316	0.161	22		45	90	32	0	61	0	7	70
4	4028	~ 0.12 ⁱ	~ 16 ⁱ	65 ^j	45	100	15	21	47	11	6	66
5	6110	0.183	24		45	66	44	<1	51	<1	5	58

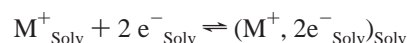
^a Electrochemical preparation of solvated electrons before addition of **1**. Electrodes used are the following: a stainless-steel cathode and a Mg anode. The supporting electrolyte $\text{Mg}(\text{BF}_4)_2$ used for the preparation of the solution of solvated electrons is prepared in situ by reduction of NH_4BF_4 . The concentration is calculated from $[\text{Mg}(\text{BF}_4)_2] = [\text{NH}_4\text{BF}_4]/2$. Procedure: The NH_4BF_4 solution is electrolyzed to prepare in situ $\text{Mg}(\text{BF}_4)_2$. After the complete reduction of NH_4BF_4 , the solution is electrolyzed again to prepare a dark-blue solution of solvated electrons of determined quantity of charge. Electrodes are removed and bromide **1** is then added. ^b Quantity of charge consumed (in Coulomb) to prepare the dark-blue solution of solvated electrons. ^c Amount of solvated electrons present in the medium before addition of the radical clock. This concentration is estimated from the mass of the Mg anode consumed during the preparation of the solvated electron solution (see experimental part). ^d Added at the same time as NH_4BF_4 . ^e Estimated from GC-MS considering the relative response factors. The amount of dimer **6** is not multiplied by two. ^f Percentage of cyclization: relative yield of products resulting from cyclization (i.e., **4**, **5**, and **6**, the amount of dimer **6** is multiplied by two). $\% \text{cycl} = [(\%4 + \%5 + 2\%6)/(\%2 + \%3 + \%4 + \%5 + 2\%6)] \times 100$. ^g Inaccurate because $[e^-]$ decreases when $t\text{-BuOH}$ is present. ^h Two mL of $t\text{-BuOH}$ in 50 mL of NH_3 . ⁱ $[e^-] = 0.38\text{ M}$ and $e^-/1 = 56$ from the mass of Mg anode consumed: these values are inaccurate because $[e^-]$ decreases when $t\text{-BuOH}$ is present. So the concentration of solvated electrons in the medium before the addition of the bromide is estimated by titration with NH_4BF_4 of a solution of solvated electrons prepared as described in entry 4 ($\text{NH}_3/\text{NH}_4\text{BF}_4/t\text{-BuOH}/4000\text{ C/no RX}$) according to $\text{NH}_4^+ + e^- = \text{NH}_3 + 1/2\text{H}_2$. This titration leads to the corrected values given in the Table ($[e^-] = 0.12\text{ M}$ and $e^-/1 = 16$). ^j Two and $1/2$ mL of $t\text{-BuOH}$ in 54 mL of NH_3 .

3. Results and Discussion

3.1. Nature of the Species Present in Solution when the Radical Clocks are Added. In the experimental part, we describe a typical experiment to create a solvated electron solution in ammonia. This solvent is characterized by its high dielectric constant ($\epsilon = 22.4$, $-33\text{ }^\circ\text{C}$) and its ability to create a cavity to solvate an electron.⁶⁰ Both qualities are important to obtain solutions of solvated electrons. Diluted solutions are blue; concentrated ones are bronze. When the concentration increases, at a given threshold, a conduction band is settled and concentrated solutions are metallic.^{61,62} Ammonia-solvated electron solutions decompose slowly because the solvated electrons react with NH_3 to yield dihydrogen and the NH_2^- anion. This decomposition is catalyzed by finely divided metal, metal oxides, traces of water, and the amide ion. It is a first-order reaction with a half-life time of about 10–20 h at $-40\text{ }^\circ\text{C}$.^{63,64}

At the magnesium anode, Mg^{++} ions are formed. These cations have such a low oxidizing strength that aqueous solutions of $\text{Mg}(\text{ClO}_4)_2$ do not react with the solvated electrons.⁴⁴ Mostafavi's group, using pulse radiolysis, was able to evidence a reaction between this cation and the solvated electron only when water was replaced by THF, ethylenediamine, or diethyl ether as solvents.^{44,46} Spectroscopic studies of the obtained transients combined with ab initio calculations led them to discard simple monovalent magnesium ions as the result of this reduction. The results observed in THF were better accounted for by the formation of an ion pair (Mg^{++} , solvated electron). An approximate way of representing this pair could be to imagine the Mg^{++} ion surrounded by a variety of ligands: THF, ClO_4^- , and the solvated electron (conceived as a large ligand). The behavior of benzene, which, depending on the temperature, the solvent, and the presence or absence of counterion, yields an actual radical anion or a pair (benzene-solvated electron) recalls, however, that the representation Mg^+ versus an ion pair (Mg^{++} -solvated electron) may vary with the conditions of observation.^{65,66} In any case, these species presents a strong reducing character: they can reduce biphenyl ($E^\circ = -2.46\text{ V}$ vs NHE)^{67–70} to its radical anion. Their rate of electron transfer to bromobenzene in THF were measured: $k = 7.1 \times 10^9\text{ M}^{-1}\text{s}^{-1}$.⁴⁵ It is not easy to extrapolate these results to ammonia.

To do so, one would have to know the solvation energies of the species involved in the relevant equilibria.^{65,71} Presently, these energies vary considerably from one author to another. A zero order approximation considering the solvation of Mg^{++} ions as the leading parameter would suggest that the solvated electron solutions of Mg^{++} in ammonia are stronger reducing agents than the ones in THF (respective dielectric constants ϵ of ammonia and THF: 22.4 and 7.52). Schindewolf proposed that, in general, the reactivity of the solvated electrons in NH_3 is appreciably lower than that in H_2O .⁷² Dilute solutions of solvated electrons in the presence of alkali metal salts have been reported to also contain pairs formed by a cation and two solvated electrons.⁷³ This situation, however, does not seem to hold in ammonia as the solvent. Because of the very high donor number of this solvent, the equilibrium



is shifted to the left.⁷⁴ The high solvation energy of Mg^{++} in ammonia probably also prevents the formation of the cation–dielectron complexes in the low concentration range.

For the experiments where the solvated electrons are cathodically generated in an ammonia solution of the radical clock (Table 2), the situation may be slightly different. In alkali metal salt solutions, cathodic generation of solvated electrons competes with electrolytic deposition of the alkali metal on the electrode. This problem was discussed in Alpatova's review on the electrochemistry of solvated electrons.⁷⁴ Unfortunately, a quantitative application of Makishima's equation⁷⁵ to magnesium is not possible because the presence of complex equilibria prevents the separate calculation of activity for the solvated electrons and the cations. In this report, we suppose that the electrolytic deposition of magnesium may be neglected.

Given the widely used method of activation of metals proposed by Rieke: reduction of MgX_2 salts by alkali metals in THF or diethyl ether yielding very fine particles of zerovalent magnesium,^{47,54} one has to consider the possibility that the solutions that react with the radical clocks contain unknown amounts of zerovalent magnesium. Under our conditions of experiment, their participation is probably negligible. Atomic magnesium reacts relatively slowly with organic halides,⁷⁶ and

TABLE 2: Reaction of Radical Clock 1 with Solvated Electrons (e⁻) in Liquid Ammonia at -40 °C ([1] = 0.0072–0.008 M, [Mg(BF₄)₂] = 0.08–0.1 M, *t*-BuOH/1 = 53)^a

entry ^b	<i>q</i> (C) ^c	color ^d	e ⁻ (generated)/ 1(consumed) ^e	conv. (%) ^f	relative yields (%) ^f				cycl. (%) ^g
					2	4	5	6	
1	31	white	2.2 ^h	29	2	81		17	98
2	60	white	1.84 ^h	67	1	90		9	99
3	95	light blue	1.95 ⁱ						
4	100	dark blue	2.06 ⁱ						
5	123	dark blue	<i>j</i>	100	1	85	1	13	99

^a Electrochemical preparation of solvated electrons in the presence of 1. Electrodes used are the following: a stainless-steel cathode and a Mg anode. The supporting electrolyte Mg(BF₄)₂ used for the preparation of the solution of solvated electrons is prepared in situ by reduction of NH₄BF₄. The concentration is calculated from [Mg(BF₄)₂] = [NH₄BF₄]/2. *t*-BuOH (2.5 mL) is added together with NH₄BF₄ in NH₃ (62 mL). Procedure: The NH₄BF₄ solution is electrolyzed to prepare in situ Mg(BF₄)₂. After the complete reduction of NH₄BF₄, bromide 1 is added and then reduced. ^b This table describes one experiment monitored with sampling (entries 1 and 2) according to the quantity of charge *q* consumed. This experiment was repeated in ammonia alone and without monitoring. The results obtained are the following: the blue color appeared after the preparation of 2 equiv. of solvated electrons, percentage of cyclization = 98% (2: 2%, 4: 93%, 6: 5%, conversion: 100%). This experiment is consistent with data of Table 2. ^c Quantity of charge consumed (in coulombs) in the presence of 1. ^d Color of the reaction mixture. ^e This column shows the number of equivalents of electrons consumed during the reduction of 1. ^f Estimated from GC-MS considering the relative response factors. The amount of dimer 6 is not multiplied by two. ^g percentage of cyclization: relative yield of products resulting from cyclization (i.e., 4, 5, and 6, the amount of dimer 6 is multiplied by two). %cycl = [(%4 + %5 + 2%6)/(%2 + %4 + %5 + 2%6)] × 100. ^h Ratio: mol of electrons generated *n* (calculated from *q* = *nF* with *F* = 96 500 C/mol of 1 consumed. ⁱ Ratio: mol of electrons generated (calculated from *q* = *nF* with *F* = 96 500 C/mol of 1 initial. The blue color suggests that the conversion was 100%. ^j At the end of the reaction e⁻/1 = 2.53. This value is not conclusive because an excess of solvated electrons was generated after the appearance of the blue color (i.e., after the end of the reaction).

an important participation of magnesium clusters in the reaction with radical clocks would be recognized by the formation of large quantities of uncyclized products.³⁶

3.2. Reactions of the Solvated Electron Solutions with Radical Clocks. Tables 1 and 2 gather the results obtained when 1-bromo-2-(3-butenyl)benzene 1 reacted with ammoniacal solutions of solvated electrons under a variety of conditions. Entries 1 and 2 in Table 1 show that, for the lowest concentrations of solvated electrons, the cyclized products are very dominant because of the cyclization of aryl radical rather than aryl carbanions (Scheme 3). Indeed, in entry 2, the addition of *t*-BuOH, a trap for carbanions, does not change the percentage of cyclized products.

Bartak et al. showed that both aryl radicals and aryl carbanions undergo cyclization in THF. In this solvent, the rate constant of radical cyclization is several orders of magnitude higher than the carbanionic one at low temperatures (-78 °C).^{28,77} At room temperature, however, this preference weakens; the overall quantity of cyclized products (4 + 5 + 6) could therefore originate from a competition of the two routes. At room temperature, the addition of 2-propanol decreases the quantity of cyclized products.^{28,77} Entries 3 and 4 show that, in our experiments, even at higher concentrations of solvated electrons, the participation of carbanionic cyclization remains negligible (unimportant effect of added *t*-BuOH on the percentage of cyclization). Under these conditions (entry 4), GC-MS analysis suggests that the formed aromatic product undergoes

TABLE 3: Reaction of Radical Clock 7 with Solvated Electrons (e⁻) in Liquid Ammonia at -40 °C ([7] = 0.007–0.008 M, [Mg(BF₄)₂] = 0.08–0.1 M)^a

entry	<i>q</i> (C) ^b	[e ⁻] M ^c	e ⁻ /7 ^c	time (min)	conv. ^d (%)	relative yields (%) ^d				cycl. (%) ^f
						8 ^e	9	10	11	
1	180	0.026	3.9	30	100	0	88	0	12	100
2 ^g	4350	0.135	18.7	45	100	4	62	25	9	96

^a Electrochemical preparation of solvated electrons before addition of 7. Electrodes used are the following: a stainless-steel cathode and a Mg anode. The supporting electrolyte Mg(BF₄)₂ used for the preparation of the solution of solvated electrons is prepared in situ by reduction of NH₄BF₄. The concentration is calculated from [Mg(BF₄)₂] = [NH₄BF₄]/2. Procedure: The NH₄BF₄ solution is electrolyzed to prepare in situ Mg(BF₄)₂. After the complete reduction of NH₄BF₄, the solution is electrolyzed again to prepare a dark-blue solution of solvated electrons of determined quantity of charge. Electrodes are removed and bromide 7 is then added. ^b Quantity of charge consumed (in coulombs) to prepare the dark-blue solution of solvated electrons. ^c Amount of solvated electrons present in the medium before introduction of the radical clock. This concentration is estimated from the mass of the Mg anode consumed during the preparation of the solvated electron solution (see experimental part). ^d Estimated from GC-MS considering the relative response factors. The amount of dimer 11 is not multiplied by two. ^e Phenol 8 could be formed from allyl phenyl ether (see text). ^f Percent of cyclization: relative yield of products resulting from cyclization (i.e., 9, 10, and 11, the amount of dimer 11 is multiplied by two). %cycl = [(%9 + %10 + 2%11)/(%8 + %9 + %10 + 2%11)] × 100. ^g Average of two experiments.

a Birch reduction to yield 5, as expected in this super-reducing medium in the presence of a proton source.^{78,79} In this experiment, GC-MS analysis also suggests the formation of butylbenzene 3; the reduction of the double bond rather than the aromatic ring is unexpected. We did not prepare an authentic sample of 1-(3-butenyl)-1,4-cyclohexadiene, but its mass spectrum should display different fragments than 3. Entry 5 corresponds to the highest concentration in solvated electrons. Compared to entries 3 and 4, this entry displays a decrease of cyclized products relative to linear ones. This suggests that a competition between reduction and cyclization rules the fate of the aryl radicals formed by the cleavage of the corresponding radical anion. Similar changes in selectivity were reported for solutions of sodium in ammonia. At very high dilution (0.003 M), the blue solution contains mainly solvated electrons. When the concentration increases, the solution becomes more and more metal-like.⁸⁰ The reduction by solvated electrons is characterized by a strong radical character; this character decreases strongly at the metal surface as shown in Table 4. Reactions with lithium metal and calcium metal in ammonia follow the same trend.^{81–84} As a first-order approximation, we neglected the contribution of H-atom abstraction from NH₃ by the aryl radical. Indeed, owing to the very strong N–H bond, NH₃ is a worse H atom donor solvent compared to other electrochemical solvents such as DMF, CH₃CN, or THF.^{85,86}

In Table 2, the reactions of 1-bromo-2-(3-butenyl)benzene 1 are performed under slightly different conditions with the aim of checking the number of equivalent electrons needed to obtain a 100% conversion of the substrate. Now, the radical clock is no longer added in a solution in which the total quantity of solvated electrons is already present. The reverse is true: one starts from an ammonia solution of the substrate 1 and Mg(BF₄)₂ in slight excess. In this solution, one progressively creates electrons at the cathode while Mg⁺⁺ is formed at the anode. The conversion increases from entry 1 to entry 5. When one is near completion of the reaction (entries 3–5), the solution turns blue. At entries 3–5, the conversion is complete and the quantity

TABLE 4: Reaction of **1** under Various Conditions

entries	[1] (M)	reductant	reductant/ 1 (eq.)	solvent	temp.	relative yields (%)		
						2	4	6
1 ^a	0.1	K (solvated electron)	2.2	NH ₃ (67%) <i>t</i> -BuOH(33%)	−28 °C	10	72	18
2 ^b	0.007	Mg (solv. el.)	3.76	NH ₃	−40 °C	2	87	11
3 ^c	0.007	K (solv. el.)	2.2	NH ₃	−40 °C	3	81	16
4 ^d	0.14	Mg	4.7	THF	rt	>99	<1	0
5 ^e	0.09	K	3.7	THF	rt	97	3	0

^a Lumps of potassium were successively added to a stirred solution of **1** in NH₃/*t*-BuOH. Each lump was added after the previous one reacted. After the addition was complete, the mixture was stirred for 2 min. 18% represents 2x the amount of dimer, see refs 38 and 93. ^b This entry corresponds to entry 1 in Table 1. ^c Reduction of **1** by the same procedure as entry 2 except that the NH₃ solution contained only 0.1 M KBr (and no Mg²⁺ salts). The electrolysis generates at the cathode solvated electron in the presence of K⁺ (formally identical to dissolution of lumps of K in NH₃) and insoluble MgBr₂ at the anode. ^d A solution of **1** (1 eq.) in THF containing 1,2-dibromoethane (0.38–0.39 eq.) and magnesium turnings was stirred for 2 h. ^e A solution of **1** (1 eq.) in THF containing *t*-BuOH (6.9 eq.) and potassium lumps was stirred for 21 h.

of consumed coulombs corresponds to a two-electron reduction of the radical clock. In this series of experiments, realized in the presence of *t*-BuOH, the percentage of cyclized products is almost quantitative.

We believe that the reaction of the radical clock with the reducing entities occurs very predominantly homogeneously, in the bulk of the solution rather than heterogeneously, in close vicinity of the cathode.

In Table 3, the reactivity of 1-(allyloxy)-2-bromobenzene **7** toward the solvated electrons is studied under conditions similar to the ones used for the reactions displayed in Table 1. The aryl radicals formed from the cleavage of the corresponding radical anion cyclize at a rate higher than $5 \times 10^9 \text{ s}^{-1}$ (30 °C), whereas the aryl radicals formed from 1-bromo-2-(3-butenyl)-benzene radical anion cyclize 1 order of magnitude slower.^{59,87–90} In agreement with these rate constants, this radical clock provides very high percentages of cyclized products (**9** + **10** + **11**).

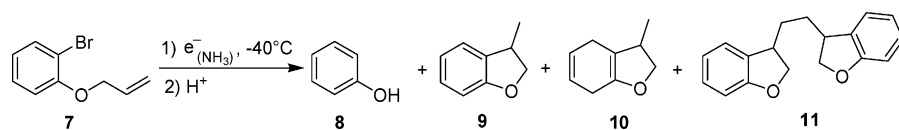
Comparison of entry 3 in Table 1 with entry 2 in Table 3 confirms this agreement. In these two entries, the increase of solvated electrons concentration (q column) leads to a decrease in the percentage of cyclized products. This corresponds to an intramolecular addition of the aryl radical to the double bond competing with its intermolecular reduction by the solvated electrons. The decrease in percentage is less important for 1-(allyloxy)-2-bromobenzene **7**. The simplest explanation of this observation could be searched in the differences of cyclization rates. It could also partly be due to differences in the oxidizing powers of the two aryl radicals, differently substituted in the ortho position. Fu et al. recently proposed a theoretical method to evaluate the E° of carbon-centered radicals.⁹¹ To our suggestion, they kindly applied this method to predict the E° value of the unsubstituted phenyl radical and its *o*-methoxyl homolog. The calculated values of E° (in CH₃CN vs NHE) are, respectively, −0.60 and −0.40 V. These values suggest that an *o*-methoxyl group increases the oxidizing properties of the phenyl radical. GC-MS analysis suggests that product **10** could correspond to the Birch reduction already observed in Table 1. The unimportant quantity of phenol **8** could be formed from the reductive C–O bond cleavage of the radical anion of allyl phenyl ether or of the starting 1-(allyloxy)-2-bromobenzene **7**, but this issue remains open.⁸⁷

3.3. Comparison with the Obtained Selectivities for the Reaction of 1-Bromo-2-(3-butenyl)benzene **1 and 1-(Allyloxy)-2-bromobenzene **7** under Different Reaction Conditions.** 1-Bromo-2-(3-butenyl)benzene **1**. The reaction of 10 mmol

of 1-bromo-2-(3-butenyl)benzene **1** dissolved in 100 mL of 67% ammonia/33% *t*-BuOH with 22 mmol of potassium (added in about 10 lumps with stirring, reflux of the solvent) yields the percentages of products displayed in entry 1 of Table 4.³⁸ The same general features are found for the electrochemical and nonelectrochemical experiments: dominance of the cyclized products over the noncyclized ones, presence of cyclic dimers. This identity substantiates the proposition made to explain the products described in Scheme 3: the crossroad where the selectivity cyclized/uncyclized is settled would be the aryl radical formed by the mesolytic cleavage of the radical anion. The solvated electrons would intervene to create the radical anion from **1** and then to compete with the intramolecular cyclization of the aryl radical. This point will be discussed further in the last paragraph of the Discussion.

The electrochemical reduction was also performed under the same experimental conditions but in the presence of K⁺ and absence of Mg²⁺ cations (entry 3 in Table 4). In this case, the electrolysis generates solvated electrons at the cathode and insoluble MgBr₂ at the anode. The reduction by solvated electrons in the presence of K⁺ or Mg²⁺ (entries 2 and 3 in Table 4) leads to a very similar proportion of compounds showing that the reductive power of the solvated electron in the presence of K⁺ or of Mg²⁺ is identical. This reduction (entry 3, Table 4) is formally equivalent to the dissolution of lumps of potassium in liquid ammonia. Overall, more cyclized products are formed in the electrochemical experiments (entries 1 and 2 in Table 1). It is difficult to extract totally unambiguous information from the comparison between these results and the one reported by Bunnett and Beckwith because our experiments were performed in more diluted solutions, in the presence of less alcohol, and at a lower temperature. For the reactions with lumps of alkali metals, Andrieux–Savéant proposed that the reaction was taking place at a distance of the metal surface where strong concentration gradients exist for the solvated electrons. The farther from this surface the radical anion was formed and cleaved, the higher the percentages of cyclized product. It was so because the strongest concentration of solvated electrons was near the metallic surface. Thus, an aryl radical born far from this surface had less chance to be reduced into an aryl carbanion and more chance to cyclize.^{92,93} The higher percentage of cyclized products obtained in our electrochemical experiments fits with this interpretation. As we will elaborate further in the last paragraph, the homogeneous solution of solvated electrons (up to 0.183 M) has a lower reducing ability than the thin layer of solution in contact with the metallic

SCHEME 4



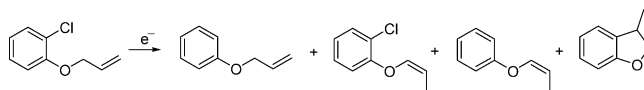
surface. When the concentration of solvated electrons increases (entries 3–5, Table 1), the percentage of cyclized products diminishes.

In a preceding work, we examined the reactivity of the same radical probe toward lumps of potassium placed in a THF solution (entry 5, Table 4).⁹⁴ Under these heterogeneous conditions (potassium is far less soluble in THF than in NH_3)⁹⁵ the behavior of 1-bromo-2-(3-butenyl)benzene **1** is strikingly different. Far less cyclized product is formed. If viewed in the solvated electron Andrieux–Savéant’s perspective, then this could mean that both the formation of the radical anion and its cleavage are taking place in very close proximity to the metallic surface. Not only the proximity would have to be higher in THF than in NH_3 but also the gradient of concentration would have to be rather high to explain the observed switch in the yield of cyclized products (3% in THF, 90% or more in NH_3). In THF, and under heterogeneous conditions, the reaction of this probe with magnesium yields less than 1% of cyclized product (entry 4, Table 4).^{36,37} In diethyl ether, this percentage increases up to 20%.³⁷ Very probably, these experiments in THF involve a reactivity of the aryl radicals near the metallic surface but do not demand the intervention of solvated electrons. Selectivity in these experiments is better treated within the framework of the kinetic zone diagrams specifically developed by the Savéant’s school.^{96–99} In this context, the active electrons are provided mainly in a heterogeneous way (see the last paragraph for further discussion).

The earliest electrochemical study of 1-bromo-2-(3-butenyl)benzene **1** was performed by Bartak’s group.^{28,77} In DMF with Bu_4NClO_4 as the supporting electrolyte, this radical probe was electrolyzed at a platinum or mercury cathode in the presence or absence of proton or hydrogen atom donor additives. At 25°C , after correction for the carbanionic participation to the cyclization, the cyclized/uncyclized ratio is, respectively, 0.04 and 0.22 at mercury and platinum cathodes without added mediator. In the presence of *m*-tolunitrile as the electron mediator, the cyclized/uncyclized ratio increased to 9. This example also clearly shows the drastic change associated with the switch heterogeneous–homogeneous electron transfer. Here, the switch is introduced by the use of redox catalysis. Redox catalysis has been used intensively to prevent the formation of carbanions when aryl radicals are formed at a cathode and should react as such to yield the desired products. One of the best studied examples is the $\text{S}_{\text{RN}}1$ reaction.^{100–103}

Kariv-Miller’s group investigated the cathodic behavior of 1-(3-butenyl)-2-fluorobenzene at mercury and lead cathodes in DMF with Bu_4NBF_4 as the supporting electrolyte. Under heterogeneous conditions, the cyclized product dominated for both cathodes: about 72% at 0°C .¹⁰⁴ This percentage could, however, be misleading. Indeed, when H_2O was added to a solution where redox catalysis is probably involved (presence of dimethylpyrrolidinium–Hg), the percentage decreased to 43%, suggesting that part of 72% is due to a carbanionic cyclization. As discussed in the last paragraph, an additional cause for this high percentage could be the longer lifetime of the aromatic fluoride’s radical anions in comparison to their bromide counterparts.¹⁰⁵ This high percentage of cyclized product would not be rationalized within the solvated electron Andrieux–

SCHEME 5



Savéant explicative framework. In the reaction of potassium with the complete series of 1-(3-butenyl)-2-halobenzenes in 67% ammonia/33% *t*-BuOH, the decrease in percentage of cyclized products follows the order $\text{I} > \text{Br} > \text{Cl} > \text{F}$.³⁸

Thus, for 1-bromo-2-(3-butenyl)benzene **1** clear-cut heterogeneous electron-transfer conditions yield at most 25% of cyclized product (reduction by magnesium in diethyl ether, electrochemical reduction at a platinum cathode in DMF).

1-(Allyloxy)-2-halobenzenes. The contrast between homogeneous and heterogeneous electron transfer is even clearer for the radical probe 1-(allyloxy)-2-halobenzenes. Sawaki’s group studied electrochemically the parent radical clock 1-allyloxy-2-chlorobenzene in 0.01 M solutions (DMF), at room temperature, and with the supporting electrolyte Bu_4NClO_4 . The cathodic electrolysis was performed under a variety of conditions: lead, platinum, copper, zinc, carbon cathodes, in CH_3CN or DMF as solvents. The obtained products are shown in Scheme 5. This reaction is dominated by the almost total absence of cyclized compounds; the highest amount is 4% at the carbon cathode in CH_3CN . At the same cathode, in DMF, no cyclized products could, however, be detected by GC–MS analysis. In this solvent, traces of the cyclized product were detected only with platinum (1%) and zinc (3%) cathodes. No cyclized product could be detected with copper, lead, or carbon cathodes when the solvent was DMF. The major products were the uncyclized compound resulting from the expected electroreductive dehalogenation and Z-enol ethers resulting from efficient isomerization induced by electrogenerated bases. The authors conclude the following: “the dechlorination occurs mostly on or near the electrode surface”.¹⁰⁶

Sawaki’s experiments must be put in perspective with Walter’s report on the reaction between magnesium metal and 1-(allyloxy)-2-iodobenzene in diethyl ether.¹⁰⁷ This author, too, could not see any traces of cyclized product. This result is even more striking for several reasons. First, Garst’s group has shown that, for the reaction of magnesium metal with the radical probe 1-bromo-2-(3-butenyl)benzene **1**, more cyclized product is obtained in diethyl ether than in THF.³⁷ Second, the *o*-allyloxyphenyl radicals should cyclize faster than the *o*-(3-butenyl)phenyl radicals.⁵⁹ Third, in the Beckwith–Bunnett experiments the iodo aromatic radical probes are the ones that yield the highest percentage of cyclized product.³⁸ This clearly points that if one has to rely on the solvated electron to explain the Beckwith–Bunnett experiments, then an heterogeneous electron transfer better explains the observed selectivities in the preparation of Grignard reagents.

Kurono et al. investigated the electrochemical generation of ortho-substituted aryl radicals using an arene mediator followed by cyclization on the double bond appropriately situated on the ortho substituents. Among the variety of structures that they studied, some were identical or very closely related to the radical probes described in the present report.^{33,35,108} The aim of their work was synthetic: they obtained higher yields of cyclized

products than those obtained using the classical radical cyclizations performed with AIBN-Bu₃SnH.¹⁰⁹

Thus, for 1-(allyloxy)-2-halobenzene clocks the contrast between the results obtained near a metallic surface and the ones obtained in the bulk with the solvated electron or an aromatic radical anion as reducing agents amplifies what has been observed with the slower (in terms of cyclization rates) 1-bromo-2-(3-butenyl)benzene **1** clock.

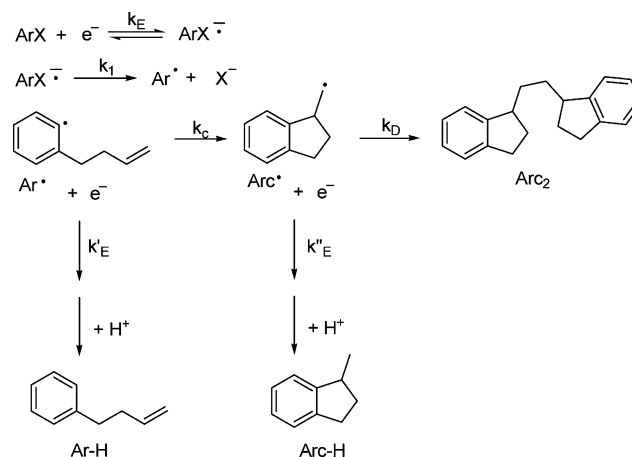
It should be emphasized, here, that if radical clocks have been used widely to gain mechanistic insight into a variety of reducing agents, then seldom have they been confronted with the solvated electrons. Only one report deals with this topic.³⁸ *The present report presents the advantage that it confronts the behavior of the same molecular probes in the presence of a metallic surface or the presence of one of the strongest reducing agents: the solvated electron.* The amazing result is that, apparently, the metallic surface displays a higher reducing ability than the solvated electron, even when this species reaches concentrations as high as 0.183 M. In the last section, we will examine why it could be so; let us briefly examine how the present results could reconcile Rieke's and Mostafavi's results.

3.4. Reconciliation of Rieke's and Mostafavi's Observations. Reduction of magnesium halides with potassium-THF or sodium-diglyme to obtain reactive powders of magnesium was an actual breakthrough in Grignard chemistry. Substrates like fluorobenzene, which had been considered inert for decades in the formation of Grignard reagents, were made reactive using such powders.⁴⁷ Later, Rieke's group brought various improvements; the experimental method that he now recommends involves a one-pot procedure using lithium rather than potassium in conjunction with a catalytic amount of naphthalene (10% by mole based on lithium) in THF under an argon atmosphere.⁵³ At first sight, these synthetic results seem at variance with the physical chemistry results reported recently by Mostafavi's group. These searchers observed that, in THF, magnesium halides do not react with solvated electrons generated by pulse radiolysis; only when the halide was replaced by a perchlorate could they observe the transient corresponding to the reduction of the salt by the solvated electron. Rather than considering the transients as actual Mg⁺ species, they preferred to describe them as (Mg⁺⁺, solvated electron pairs). These results point at a very low intrinsic oxidizing ability of Mg⁺⁺ salts. This very low oxidizing power is very probably connected to the strong solvation of Mg⁺⁺ ions: in water where this solvation is the strongest, even magnesium perchlorates do not react with pulse radiolytic generated solvated electrons.^{44–46,110} If magnesium dicationic species are so reluctant to accept an electron, then how could we explain the formation of activated zerovalent magnesium by reduction of MgX₂?

Given the present report, a possible rationalization could be that Rieke's experiments involve an heterogeneous electron transfer whereas Mostafavi's ones involve an homogeneous one. In Rieke's experiments, Mg⁺ species would be formed in the close vicinity of a heterogeneous reducing agent whose intrinsic reducing ability is higher than the solvated electron. These transient Mg⁺ species, which display very strong reducing properties, would then produce zerovalent magnesium via disproportionation.^{111–115}

3.5. Homogeneous versus Heterogeneous Electron Transfer Relevant to Selectivity in Grignard Reagent Formation. A Quantitative Electrochemical Approach. *Estimation of the Relative Rates of Cyclization of the Radicals Formed by the Cleavage of the Radical Anions of 1 and 7.* The reaction

SCHEME 6



mechanism under scrutiny is presented, in a simplified version, in Scheme 6.

where k_1 represents the ArX radical anion fragmentation rate constant, k_c is the radical cyclization rate (taking at -40°C , $k_c \approx 9 \times 10^7 \text{ s}^{-1}$ for substrate **1**, and $k_c \approx 1.5 \times 10^9$ for substrate **7**).^{89,90} k_E is the rate constant for the substrate reduction, k'_E and k''_E are the rate constants for the reduction of, respectively, the uncyclized, Ar[•], and cyclized, Arc[•], radicals and k_D is the rate constant for the dimerization of Arc[•]. The electron transfers to the molecules can be induced either homogeneously, in solution by an electron donor (such as the solvated electron or a redox mediator as discussed later), or heterogeneously from the encounter of the reducible species with the metallic surface of an electrode. Because generally aryl radicals Ar[•] (and Arc[•]) are reduced much more easily than their ArX parents, when ArX^{•-} cleaves quickly, under homogeneous (respectively heterogeneous) conditions the intermediate aryl radicals are reduced homogeneously (respectively heterogeneously) at rates close to the diffusion limit.

When the reduction is performed homogeneously, for example in a solvated electron solution, all of the electron-transfer steps are homogeneous reactions of, respectively, the substrate, the uncyclized radical, and the cyclized radical with the solvated electron at bimolecular rate constants, k_E , k'_E , and k''_E , respectively, expressed in $\text{M}^{-1} \text{ s}^{-1}$. When the reduction is performed heterogeneously by a surface, the electron-transfer reaction rate refers to unit surface area, in $\text{mol s}^{-1} \text{ cm}^{-2}$; hence, the heterogeneous electron-transfer rate constants, k_E , k'_E , and k''_E , are expressed in cm s^{-1} . This could seem to be a rather peculiar dimension. It is because one has to relate a flux per unit area in terms of a concentration per unit volume.¹¹⁶

The high yields of cyclized radical clock obtained under homogeneous conditions clearly contrast with those obtained when the reduction was induced heterogeneously. Entries 1–3 of Table 4 are representative of the same homogeneous induction of the reduction. When this homogeneous reduction is induced by solvated electrons coming from alkali metals dissolution in NH₃, or from the mixing of the substrate into a solvated electron solution, the relative yields of products should then be rationalized by the Andrieux–Savéant formalism.^{92,93} This formalism describes quantitatively the product distribution obtained in reactions occurring during the mixing of two reactants under stirring, in our case the solvated electron and the ArX substrate. The model is based on the mathematical resolution of the diffusion equations pertaining to the substrate, the solvated electron, and the different reaction products, Ar–H, Arc–H, and Arc₂, in order to assess their respective concentrations in

the solution and therefore evaluate the product distribution. All of the reaction intermediates are considered to obey the steady-state approximation. The use of this formalism allows the estimation of the pertinent rate constants of the substrate reduction mechanism from the product distribution.

A detailed analysis of the mathematical model adopted can be found in the original Andrieux–Savéant papers. Briefly summarized, it demonstrates that the reaction between the ArX molecule and the solvated electron and therefore all of the successive reactions proposed in Scheme 6 take place in a very thin reaction layer located within the layer where the reactants (ArX and the solvated electron) are mixed. Because the reaction between the solvated electron and ArX is fast, (i) this reaction layer is very thin compared to the mixing layer, and (ii) the amount of solvated electron and ArX is small in the reaction layer, as they react altogether. Moreover, the faster this homogeneous electron-transfer reaction (the higher the k_E), the more efficient the solvated electron depletion in the reaction layer and then the smaller the concentration of solvated electron within the reaction layer. According to Scheme 6, the obtention of the different competing reaction products are intimately coupled to the reduction of the radical intermediates, k'_E and k''_E , by the solvated electrons. Therefore, it is expected that the distribution of these different reaction products is dictated by the solvated electron availability in the reaction layer, and thus by the value of the substrate reduction rate constant, k_E .

To be more specific, the various amount of uncyclized, Ar–H, cyclized, Arc–H, and dimeric, Arc₂, products are shown to depend on two competing dimensionless scaling kinetic parameters, σ and ρ , obtained from the scaling of the diffusion-reaction problem according to the Andrieux–Savéant model of the process. These scaling parameters characterize, respectively, the competition between the radical cyclization versus its possible reduction and the competition between the cyclized radical reduction versus its dimerization. They are obtained from the mathematical resolution of the diffusion-reaction problem, but they can also be estimated from a more elementary scaling analysis of the kinetic process proposed by Amatore.^{97,98} This approach consists of evaluating the average concentration, in the reaction layer, of the key species (here radical species) involved in the two competing ways under consideration. The lower the key species concentration according to one route, the more efficient the route.

For example, in the special case of the cyclization versus reduction competing paths, the key species of the competition is the linear radical, named Ar•. Its average concentration in the reaction layer, if one considers that the cyclization is the major pathway, named (Ar•)_{cyc} is given by a steady-state approximation: $k_c(\text{Ar}^\bullet)_{\text{cyc}} = k_1(\text{ArX}^{\bullet-})$ where (ArX•[−]) is the average concentration of ArX•[−] in the reaction layer. It ensues that $(\text{Ar}^\bullet)_{\text{cyc}} = k_1(\text{ArX}^{\bullet-})/k_c$. If, now, the homogeneous reduction step is the major path, then the average concentration of Ar• according to this path, named (Ar•)_{red}, is given by $k'_E(\text{Ar}^\bullet)_{\text{red}}C_e = k_1(\text{ArX}^{\bullet-})$ where C_e is the concentration of the solvated electron in the reaction layer, and $(\text{Ar}^\bullet)_{\text{red}} = k_1(\text{ArX}^{\bullet-})/k'_EC_e$. One can then define from this approach the same scaling dimensionless parameter σ obtained by Andrieux–Savéant from the scaling of the diffusion-reaction process. This σ parameter reflects the competition between cyclization and reduction of the linear aryl radical. It may be recalled that this parameter is not the ratio of cyclized to reduced product but an image of the competition between those two steps: the higher σ , the more favorable the cyclization step, and then the higher the cyclization

yield, the lower the yield of the uncyclized product Ar–H. The parameter σ is given by

$$\sigma = \frac{(\text{Ar}^\bullet)_{\text{red}}}{(\text{Ar}^\bullet)_{\text{cyc}}} = \frac{k_c}{k'_EC_e} = \frac{k_c}{k'_E[e]^{2/3}D^{1/3}} \quad (1)$$

where C_e , the concentration of the solvated electron in the reaction layer is expressed, in the right-hand side of eq 1 as a function of k_E , the substrate reduction rate constant, D , the species diffusion coefficient ($3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in NH_3 at -40°C), $[e]$, the concentration of the solvated electron in the solution bulk, and δ , the thickness of the diffusion layer (typically about 10^{-3} cm).

Similarly, the competition between the different steps of reduction and dimerization of the cyclized aryl radical, Arc•, results from the average concentration of the cyclized aryl radical. For the sake of simplicity, let us assume that the cyclization corresponds to the major path of the aryl radical, Ar•. When dimerization is the main evolution path of the cyclized radical, named Arc•, at steady state, one could write $2k_D(\text{Arc}^\bullet)_{\text{dim}}^2 = k_c(\text{Ar}^\bullet) = k_1(\text{ArX}^{\bullet-}) = k_EC_eC_{\text{ArX}}$. In the center of the reaction layer the solvated electron and the substrate concentration, C_{ArX} , are equal, then $(\text{Arc}^\bullet)_{\text{dim}}^2 = k_EC_e^2/2k_D$. However, if the cyclized radical is mainly reduced, then $k''_E(\text{Arc}^\bullet)_{\text{red}}C_e = k_c(\text{Ar}^\bullet) = k_1(\text{ArX}^{\bullet-}) = k_EC_eC_{\text{ArX}}$ and $(\text{Arc}^\bullet)_{\text{red}} = k_EC_e/k''_E$. Again, one could define from this approach a scaling dimensionless parameter ρ identical to that obtained by Andrieux–Savéant from the scaling of the diffusion-reaction process. This ρ parameter, which reflects the competition between reduction and dimerization of the cyclized aryl radical, is then given by

$$\rho = \left(\frac{(\text{Arc}^\bullet)_{\text{dim}}}{(\text{Arc}^\bullet)_{\text{red}}} \right)^2 = \frac{k''_E{}^2}{2k_Dk_E} \quad (2)$$

Here again, it may be recalled that this parameter is not the ratio of reduced cyclized to dimerized products but an image of the competition between those two steps: the higher ρ , the more favorable the reduction of Arc• into Arc–H and then the lower the yield of dimerized product, Arc₂. The substrate reduction rate constant, k_E , intervenes in the competition parameter between dimerization and reduction of Arc•. It indicates that the fate of the cyclized radical is also dependent on the preceding reduction of the substrate.

This result could appear as counter-intuitive because the molecular partitioning of the radicals into products occurs after the reduction of the starting substrate. Actually, this presence of k_E in eqs 1 and 2 agrees with the experimental observations. Both Bunnett and then Beckwith and Bunnett observed leaving group effects on the selectivity of products.^{38,117} It is a strong point of the Andrieux–Savéant treatment that it accounts for these observations. In terms of physical sense, this dependence of k_E in eqs 1 and 2 follows from a simple fact: the selectivity is settled in a nonhomogeneous medium. Depending upon the kinetic oxidizing power of the starting substrate ($\text{I} > \text{Br} > \text{Cl} > \text{F}$), the radical anion will be created and react in a different part of this nonhomogeneous medium. If the radical anion cleaves in a part of the solution richer in solvated electron, then the radical born from its cleavage will be reduced faster. This simplified picture is more thoroughly detailed in Andrieux–Savéant reports.^{92,93}

Once those kinetic competition parameters are estimated, it is tempting to use them in order to extract kinetic rate constants. The strategy then, consists of estimating σ and ρ by comparing

the experimental yields of the uncyclized product and the relative amount of dimeric product with the theoretical variations of those quantities with σ and ρ . Schematically, the yield of uncyclized product $R_{\text{uncyc}} = [\text{Ar-H}]/([\text{Ar-H}] + [\text{Arc-H}] + 2[\text{Arc}_2])$ depends solely on the parameter σ and the variation of R_{uncyc} is a decreasing function, S-shaped, of $\log \sigma$: $R_{\text{uncyc}} \rightarrow 1$ when $\sigma \rightarrow 0$ ($\log \sigma \rightarrow -\infty$) and $R_{\text{uncyc}} \rightarrow 0$ when $\sigma \rightarrow +\infty$ ($\log \sigma \rightarrow +\infty$). The estimation of σ is straightforward from the abacus presented in Figure 2 of ref 93 and the experimental yield of uncyclized product. The estimation of ρ is obtained from the relative amount of dimer product and the corresponding abacus. Now the relative amount of the cyclized products that are reduced or that dimerize, $R_{\text{cyc}} = [\text{Arc-H}]/([\text{Arc-H}] + 2[\text{Arc}_2])$, depends on both σ and ρ . The estimation of ρ then requires the knowledge of σ and of the experimental value R_{cyc} . The abacus presented in Figure 3 of ref 93 is not correct because it does not represent the relative yield of cyclized product ($R_{\text{cyc}} = [\text{Arc-H}]/([\text{Arc-H}] + 2[\text{Arc}_2])$) as a function of the parameters ρ and σ as stated in the text. Indeed, for example, R_{cyc} should be increasing while ρ is increased. This abacus has been recomputed, and its correct form is given in Figure 1 (Supporting Information). The curves represent the variation of R_{cyc} as an increasing S-shaped function of $\log \rho$ for different values of σ : $R_{\text{cyc}} \rightarrow 0$ when $\rho \rightarrow 0$ ($\log \rho \rightarrow -\infty$) and $R_{\text{cyc}} \rightarrow 1$ when $\rho \rightarrow +\infty$ ($\log \rho \rightarrow +\infty$) and, for a given ρ value, when σ increases R_{cyc} decreases. The reinterpretation of the data of ref 93 with Figure 1 in the Supporting Information leads to the exact values of the physical parameters given in ref 93.

From the value of ρ obtained with this theoretical treatment (Table 5, Supporting Information), an estimate of k_E might be obtained assuming that the other reduction steps and the dimerization step are at the diffusion rate ($k'_E = k''_E = k_D = k_{\text{diff}}$). Owing to liquid ammonia's properties: rather low viscosity, $\eta = 0.027$ cp at -40 °C^{118,119} (compare to $\eta = 0.092$ cp for DMF at 20 °C) diffusion coefficient¹²⁰ and then the diffusion rate, k_{diff} , in this solvent are quite high and $k_{\text{diff}} = 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.¹²¹ The rate constant of reduction of the substrate by the solvated electron is about 1 order of magnitude lower than the diffusion limit, in good agreement with the observation of the reduction of the substrate in DMF^{28,77} or of bromobenzene at potentials very close to the potential of generation of solvated electrons (or solvent discharge).⁹³ Using the value of k_E obtained, one could estimate the standard reduction potential of the two substrates from the energy dependence of the electron-transfer rate constant by Marcus theory.¹²² For near diffusion-limited rate, the electron transfer is controlled by activation and/or diffusion and its rate constant k_E is given by

$$\frac{1}{k_E} = \frac{1}{k_{\text{diff}}} + \frac{1}{Z^{\text{hom}} \exp\left(-\frac{F\Delta G^{\circ,0}}{RT} \left(1 + \frac{E_E^0 - E^0}{4\Delta G^{\circ,0}}\right)^2\right)} \quad (3)$$

where Z^{hom} is the bimolecular collision frequency equals to $3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, $\Delta G^{\circ,0}$ is the intrinsic barrier of the homogeneous electron transfer (about 0.2 eV for aromatic molecules)^{105,122} and E_E^0 and E^0 are the standard reduction potentials of the solvated electron and the substrate, respectively. With this equation, one estimates that the two investigated substrates have standard reduction potentials about 0.25 V more positive than that of the solvated electron, say about -2.15 V versus Ag/Ag⁺ (equivalent to -2.62 V vs SCE in DMF at room temperature). This is consistent with (1) the observation of the reduction of **1** at a potential close to, but more positive than the solvent

discharge,^{28,77} but also with (2) the value of -2.44 V versus SCE for the standard reduction potential of bromobenzene in DMF.¹⁰⁵

Then, from the values of σ one could estimate the diffusion layer thickness taking $k_c = 9 \times 10^7 \text{ s}^{-1}$ for **1** and $k_c = 1.5 \times 10^9 \text{ s}^{-1}$ for **7**. It is about 10^{-3} cm (Table 5, Supporting Information), in good agreement with values estimated from preparative scale $S_{\text{RN}}1$ reactions in liquid NH_3 , which lends confidence in the analysis of those results within this theoretical formalism.¹²³ The use of such an available theoretical model is then satisfying for better insight into the kinetics of cyclization of radical probes from the values of the kinetic parameters σ and ρ . The unknown value of the cyclization rate of a "new" radical probe (for example **7**), $k_{c,u}$ can be obtained by comparison to that of a known one, say substrate **1**, $k_{c,1}$, and from combination of the expressions of σ and ρ in eqs 1 and 2 as

$$k_{c,u} = k_{c,1} \left(\frac{\sigma_u}{\sigma_1} \left(\frac{\rho_u}{\rho_1} \right)^{1/3} \right)^{1/3} \quad (4)$$

When this equation, using the values of σ and ρ displayed in Table 5 (Supporting Information) for comparable values of solvated electron concentrations, is applied to compare the cyclization rate of probes **7** and **1**, it leads to $k_{c,7}/k_{c,1} = \sigma_7 \rho_7^{1/3} / (\sigma_1 \rho_1^{1/3}) \approx 14$, in reasonable agreement with the expected ratio of 18.⁸⁹

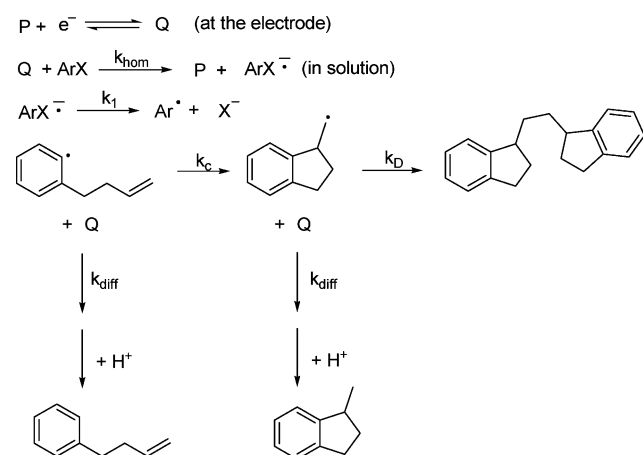
Ratios of Cyclized/Uncyclized Products when the Radical Clocks are, Respectively, Reduced Homogeneously or Heterogeneously. The experimental results reported in the present paper clearly illustrate the contrasting selectivities obtained when the reducing electrons are brought homogeneously or heterogeneously to the substrate. An important trend in organic chemistry using zerovalent metals has been the improvements in yields made possible by the addition of mediators to the reacting medium. This trend has been especially important in lithium chemistry.^{124–131} It is interesting to situate these works within the preceding electrochemical approach. When the homogeneous reduction is performed by an electrogenerated redox mediator (a radical anion formed at a large cathode for example), a similar theoretical analysis can be considered.^{123,132,133} A dimensionless scaling parameter σ' may be obtained analogously from Amatore's approach that characterizes the competition between the radical cyclization and its homogeneous reduction¹²³

$$\sigma' = \frac{k_c}{k_{\text{diff}}(Q)} \approx \frac{k_c F S \sqrt{2k_{\text{hom}} D C_0}}{k_{\text{diff}} i} \quad (5)$$

where $F = 9.65 \times 10^4 \text{ C mol}^{-1}$ and (Q) is the average concentration of the reduced form of the redox mediator in the reaction layer. (Q) can be estimated from its rate of formation, at the electrode of surface area S , which is estimated from the current i flowing at the electrode during the formation of Q and from k_{hom} , the rate constant for the homogeneous reduction of the substrate (concentration C_0) by the reduced form, Q , of the redox mediator P according to Scheme 7. The reduction of the intermediate radicals (far better oxidants) is also achieved homogeneously but at the diffusion rate ($k_{\text{diff}} = 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

This scaling parameter σ' is similar to the parameter σ proposed in the Andrieux–Savéant description of the solvated electron dissolution.⁹² As mentioned previously, the amount of Q available for the reduction of the two intermediate radicals (which occurs at diffusion rate, k_{diff}) depends on the efficiency of the homogeneous reduction of the substrate. It indicates that

SCHEME 7



the percentage of cyclization increases when the cyclization rate increases. It also increases with (1) the rate k_{hom} of the homogeneous substrate reduction (not to be confused with the rate constant of reduction of the aryl radical formed from the cleavage of $\text{ArX}^{\bullet-}$), (2) the substrate concentration C_0 , and (3) the diffusion coefficient D . It decreases when the redox mediator generation rate (a heterogeneous electron transfer), that is, the electrode current, increases. These variations hold for a stoichiometric amount of mediator as used in Cohen's group for reductive lithiation.¹²⁷

This aspect is particularly important to visualize; it points out the difference between the homogeneous and heterogeneous induction. The homogeneous parameters for the cyclization versus reduction of the radical σ and σ' show the easier the reduction of the starting substrate ArX by the homogeneous electron donor, the higher the cyclization of the radical. It could seem paradoxical that the strongest reducer's homogeneous electron donor favors the cyclization instead of reduction of the radical. Actually, this points out the drawback of the homogeneous induction: the electron transfers are performed by diffusing molecules. Then, if the first homogeneous electron transfer is very efficient, then less electron donors in the solution close to the formed radical will be available to perform the second electron transfer, favoring the radical cyclization. The situation would be more complex if the mediator was a dianion, particularly if the monoanionic form is a better reducing agent than the dianionic one.^{131,134,135}

When the substrate is introduced in great excess compared to the redox mediator (so-called catalytic in Yus' group¹²⁹), the percentage of cyclization is given by

$$\% \text{Cyc} = \sigma' \ln(1 + 1/\sigma') \quad (6)$$

Typically, from this variation, more cyclized products, Arc-H and Arc_2 (i.e., >50% of cyclized product or $\% \text{Cyc} > 0.5$), begins to be obtained for values of $\sigma' > 0.4$. This means that for a substrate concentration of 0.01 M and diffusion coefficient $10^{-5} \text{ cm}^2 \text{ s}^{-1}$, for electron current densities of 10 mA/cm^2 , values of k_{hom} such as $k_c k_{\text{hom}}^{1/2} > 0.1 k_{\text{diff}}$ or $k_{\text{hom}} > 0.01 (k_{\text{diff}}/k_c)^2$ are expected. Typically, for the cyclization of the 2-(3-butenyl)-phenyl radical, the cyclization (taking $k_c = 4 \times 10^8 \text{ s}^{-1}$ at 25°C and $k_{\text{diff}} = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) is already favored for $k_{\text{hom}} > 6 \text{ M}^{-1} \text{ s}^{-1}$.

Therefore, if the reduction of **1** is induced by a redox mediator, in a homogeneous fashion, then it will lead principally to the cyclization of this radical when its formation (via the radical anion of **1**) is achieved exclusively by homogeneous means.

Now, for slower cyclization (or rearrangement) rates, such as those of alkyl halide radical clocks ($k_c \approx 10^5 \text{ s}^{-1}$) the cyclization will be favored (i.e., >50% of cyclized product) for higher homogeneous rate constants such that $k_{\text{hom}} > 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (taking $k_{\text{diff}} = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). A caution, however, to be kept in mind when zerovalent metals like lithium are considered, is that a major part of the cyclized products may originate from a carbanionic cyclization.¹³⁶

Let us, now, compare the dimensionless scaling competing parameter that predicts the competition of the cyclization versus reduction within the homogeneous reduction performed by a redox mediator and the heterogeneous case. For alkyl halides, the equivalent scaling parameter proposed by Garst in its original expression

$$\sigma''_{\text{alk}} = \sqrt{k_c \tau_R} \quad (7)$$

indicates that what counterbalances the radical cyclization is its lifetime before it can react at the metal.¹³⁷ This lifetime of the radical that escapes from the metal surface by diffusion, with the diffusion coefficient D , before it can return to this surface and react with it at the rate k_{el} (rate constant of the heterogeneous electron transfer) is $\tau_R = D/k_{\text{el}}^2$. Garst then proposed that every radical clock should react with the metallic surface with similar reaction time ($\tau_R \approx 10^{-7} \text{ s}$). This assumption is reasonable because this reaction time reflects the rate of the transfer of one electron from the metal to the radical species. As a rough approximation, neglecting the fact that aryl radicals are better oxidizing agents than alkyl ones, this rate could be supposed as not dependent on the structure of the substrate; a reasonable value could be $k_{\text{el}} \approx 10 \text{ cm s}^{-1}$.⁸⁷

However, Garst did not consider the existence of radical anion species as reaction intermediates. When a radical anion with a definite lifetime is formed as an intermediate on the route leading to the carbon-centered radical, the situation is changed. In this case, the Amatore's approach precedently used for the definition of the appropriate dimensionless competing scaling parameter can be applied to rule out this situation. It requires the comparison of the uncyclized aryl radical average concentration, (Ar^{\bullet}) when it gets either mainly reduced or mainly cyclized. If one considers that the cyclization is the major pathway, then $(\text{Ar}^{\bullet})_{\text{cyc}}$ is again $(\text{Ar}^{\bullet})_{\text{cyc}} = k_1(\text{ArX}^{\bullet-})/k_c$ where $(\text{ArX}^{\bullet-})$ is the average concentration of $\text{ArX}^{\bullet-}$ in the reaction layer. If the heterogeneous reduction is now the major pathway, then the rate of chemical disparition of $\text{ArX}^{\bullet-}$ is equal to the rate of chemical apparition of Ar^{\bullet} and then the average concentration of Ar^{\bullet} should be equal to that of $\text{ArX}^{\bullet-}$ in the reaction layer: $(\text{Ar}^{\bullet})_{\text{red}} = (\text{ArX}^{\bullet-})$. The cyclization versus heterogeneous reduction of the radical is then governed by the new scaling competing parameter σ'' :

$$\sigma'' = \left(\frac{(\text{Ar}^{\bullet})_{\text{red}}}{(\text{Ar}^{\bullet})_{\text{cyc}}} \right)^{1/2} = \sqrt{\frac{k_c}{k_1}} \quad (8)$$

Equation 8 may, at first view, look unusual. Generally, rate constant ratios pertain to the partitioning of a single reactive intermediate; here, k_c describes a cyclization of the linear radical formed by the cleavage of a radical anion and k_1 describes the cleavage of this radical anion. The description of the succession of events for two extreme cases should clarify the physical meaning of this equation. If k_1 is so large that the cleavage occurs in the close vicinity of the surface, then the linear radical will be born in such a highly reducing medium that the cyclization will have very low chance to compete with its

immediate reduction. Alternatively, if k_1 is sufficiently small (long-lived radical anion), then the radical anion will have time to diffuse away from the surface. Therefore, its cleavage will occur far enough from the surface to produce a linear radical in a far less reducing medium. Now, the competition between the cyclization of this radical and its reduction will become much more feasible.

The reaction that counterbalances the cyclization of the linear neutral radical is the radical anion fragmentation rate constant k_1 ; the yield of cyclized product is now

$$\%Cyc = \sigma''/(1 + \sigma'') \quad (9)$$

The expression of the competition parameter remains expressed in an expression very similar to that proposed by Garst (we have chosen to express σ'' as the square root of the concentration ratios in order to compare it better to the parameter derived from Garst, σ''_{alk}). But, if such a radical anion is formed, then the radical issuing from the fragmentation of this radical anion may be generated in solution "far" from the metal surface. In this case, what counterbalances the cyclization of the radical is no longer the lifetime of the aryl radical but the lifetime of the radical anion that gives birth to the radical. The reaction time τ_R now becomes the radical anion lifetime $\tau_R = 1/k_1$ and then depends on the chemical structure of the substrate. Therefore, contrary to what was proposed by Garst, the cyclization of substrates that generates radical anions of given lifetimes can involve a reaction time τ_R much different from those observed when radical anions are not considered.

This argument is quite relevant for the rationalization of selectivities in Grignard reagent formation. First, when comparing homogeneous and heterogeneous induction, one sees that the importance of the first reductive step only intervenes in the case of the homogeneous induction. This follows from the fact that the rate of reduction is limited by the transport or the availability of the electron carrier only when this electron carrier is in the solution (eq 5). Second, in the heterogeneous case, the difference between alkyl and aryl halides concerns principally the formation or not of a radical anion. Indeed, during the alkyl halide reduction radical anions are not formed¹²² (except, possibly, at very low temperatures),¹³⁸ Therefore, the cyclization competes with the radical reduction at the metal. Conversely, when aryl halides are considered a radical anion may be formed; now, the cyclization competes with the radical anion fragmentation (eq 9). The case of aryl iodides is certainly ambiguous because their reduction could or not involve the passage by a radical anion and a situation intermediate between the alkyl and aryl halides could be observed.^{139,140}

To illustrate this discussion, let us compare the ratio of cyclized/uncyclized products for a heterogeneous electron transfer on alkyl and aryl radical clocks supposed to produce radicals whose rate constants of cyclization are identical. Taking k_{el} , the rate constant of heterogeneous electron transfer to the alkyl radical, as 10 cm s^{-1} , one may transform it to make it comparable to a first-order chemical decomposition rate constant, k (k is physically similar to the radical anion cleavage rate constant k_1 defined in Scheme 6) using

$$k = (k_{el})^2/D \quad (10)$$

With $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, one obtains $k = 10^7 \text{ s}^{-1}$. For the aryl radical clock, the step that competes with the cyclization of the radical is the cleavage of the radical anion. For many halogenoaromatic radical anions, this rate constant of cleavage is higher than 10^7 s^{-1} .⁶⁶ Therefore, within our approach one

would expect that out of the two radical clocks the alkyl one should yield a higher cyclized/uncyclized ratio than the aryl one; in agreement with the experimental data. For more stable radical anions ($k_1 < 10^7 \text{ s}^{-1}$), the situation becomes more complex and one has to resort to kinetic zone diagrams.^{96–98}

The fragmentation rate of the radical anion of **1** can be estimated from the yield of cyclized product obtained from the direct reduction of **1** at platinum ($\% \text{ cyc} = [\text{Arc-H}]/([\text{Ar-H}] + [\text{Arc-H}]) = 0.16$),^{28,77} and a value of $k_1 = 10^{10} \text{ s}^{-1}$ is obtained (if $k_c = 4 \times 10^8 \text{ s}^{-1}$ at 25°C). The lifetime of the radical anion of **1** is within the subnanosecond ($\tau_R = 1/k_1 = 10^{-10} \text{ s}$), a lifetime 3 orders of magnitude shorter than the characteristic time of $0.1 \mu\text{s}$ lifetime proposed by Garst for the radicals formed from alkyl halides.¹³⁷ The existence of a radical anion is not the panacea; their involvement could be only one of the reasons contributing to explain the very low percentage of cyclization of aryl halide radical clocks engaged in Grignard reactions despite the high cyclization rate constants of the relevant aryl radicals. However, it opens investigation routes not discussed until now.

4. Conclusions

This study of the same radical clocks both electrochemically and in their reactions toward metal surfaces (magnesium or potassium) shows the drastic difference in terms of selectivity between homogeneous and heterogeneous electron transfer. This difference is striking because the homogeneous reduction is performed with one of the best reducing agents: the solvated electron. Even at concentrations in the range of 0.183 M , this reducing agent is less efficient to reduce an aryl radical than the cathode or the magnesium metallic surface in their close spatial vicinity. This observation provides a basis to rationalize the remarkable Rieke's method for the preparation of very active metal slurries.

The electrochemical modeling in terms of kinetic treatment of redox catalysis brings fresh views in the rationalization of the overall selectivity observed in Grignard reagent formation. This is a particularly important point for the two fields where this bridge has been settled for the first time. On the side of the Grignard reagent formation and, possibly, for other reactions involving the direct reaction of a metal with an organic substrate, the rationalization of selectivity may demand the application of concepts born in double-layer electrochemistry. In these concepts, the role of diffusion rates is important; this parameter was already underlined in early contributions from Whitesides's group.^{141–143} The difference, in terms of rationalizing selectivity, comes to introducing a new dimension. In the vicinity of the metal surface, every point of the solution starting from the metal surface is equivalent to a new nanosized reaction vessel. In each vessel, the conditions of concentration of substrate, reactive intermediates, and product are different. The overall selectivity results from the composition of all of these nanovessels. Fortunately, the electrochemical models of such a situation have been realized by appropriate mathematical treatments where concentrations are derived with respect to both time and space.^{96–98} Understanding of selectivity for one of the oldest and most used reactions in synthesis demands the introduction of concepts born in the most modern approaches of electrochemistry.

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Supporting Information Available: Additional experimental details and kinetic parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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