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Recueil Review

Review on the electrochemistry of solvated electrons. Its use in hydrogenation of monobenzenoids

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1. Introduction

Electrochemical generation of solvated electrons (e_s^-) was first observed by Cady in 1897[1] who found that when a sodium salt solution in liquid ammonia is electrolysed, a blue coloration is observed at the cathode. The kinetics of this process were investigated quantitatively for the first time by *Laitinen* and *Nyman*[2]. This work remained unnoticed until, almost simultaneously, three groups of researchers[3–5] started systematic studies into the kinetics of the e_s^- electrode reaction.
In addition to the features common to all electrode reactions, the electrochemistry of the e_s^- has its own distinctive characteristics. These are primarily related to the specificities of the state of excess electrons in polar liquids. Unlike other particles, electrons can exist both in localized and delocalized states.
Undoubtedly, knowledge of the electrochemical e_s^- generation mechanism is of fundamental importance, since it can give insight into general electrochemical processes and kinetics. In an e_s^- reaction no 'heavy' particle acts as an electron donor or acceptor; in this sense the electrochemical generation of e_s^- is the 'most simple electrode process'.
In practical terms e_s^- have the same reducing power as the alkali metals: e_s^- obtained by dissolving alkali metals in liquid ammonia or similar solvents are now used for the reduction of organic compounds.
The use of electrochemically obtained e_s^- avoids inconveniences associated with the use of alkali metals and moreover, their generation has several distinctive features. For example, compared to direct cathodic reduction, larger current densities can be used due to the high e_s^- diffusion coefficient.
A typical characteristic of e_s^- is their ability to react with compounds which are not reduced at all at a cathode, for example benzene. 1,4-cyclohexadiene and/or cyclohexene are common products. In this paper, the electrochemistry of the e_s^- is reviewed and the application of e_s^- as reducing agents for benzenoid compounds is discussed.

2. Electrochemical aspects of the solvated electron

2.1 History

Since the discovery of the hydrated electron by *Hart* and *Boag*[6], the theoretical[7–10] and experimental[11–13] study of electrons in liquid media has become an active area of research.
Excess electrons in liquids can exist in a variety of states. These may be classified broadly into either localized or extended states, depending on the size of the electron wave function. The lowest extended state is at the bottom of the conduction band of the liquid. This state is empty in a pure liquid and is occupied when excess electrons are present[14].
Not all excess electrons occupy the conduction band, in which the wave function is extended. In many cases the electrons are trapped. In the trapped state the electron wave function is localized in space. There are two general types of trapped electrons: presolvated and solvated. The former implies localization of the electron in a preexisting site or cavity without any relaxation of the solvent molecules. The latter implies solvent molecules having acquired their equilibrium configuration, corresponding to a lower energy state.
It is generally believed that, upon injection into a polar liquid, the electron goes through three distinct states. The first state corresponds to the unsolvated, essentially 'free' electron, scattering through the liquid. Once enough energy has been dissipated, the electron becomes presolvated (the thermalization time is expected to be much less than a picosecond) and finally solvated. Only the last two intermediates are believed to contribute to the near-infrared and visible absorption bands observed in experimental studies of electron solvation.
Since the 1940s theoretical models have been proposed to explain the optical absorption of e_s^-. *Ogg*[15] developed the first quantitative theory to explain the states of an electron in ammonia. In this theory it is assumed that a spherical cavity is formed around the electron. *Davydov*[16] was the first to describe e_s^- in ammonia using the *Landau-Pekar* theory[17,18] of large polarons: by its negative charge, an electron polarizes surrounding solvent molecules with a dipole moment, and eventually, the electron is trapped in the potential well arising from these oriented solvent molecules. Within the framework of the *Davydov-Deigen*[19] theory, which has been developed in contrast to *Ogg*'s cavity theory, it is possible to obtain a number of characteristics of e_s^- in ammonia consistent with experimental data. In addition to the polaron model, other theories (the semi-continuous model[20], the cluster theory[21]) have been introduced and developed. Reviews of these theories[7,8] have been presented in the literature.

2.2 The electrochemical generation of e_s^-

The e_s^- in the condensed phase can be obtained by several methods[22-29]:

- by the radiation-chemical method (radiolysis), in which electrons detached from molecules, ions or atoms by ionizing radiation, form e_s^-;
- by the photochemical and the photoelectrochemical method;
- via the reaction of atomic and/or molecular hydrogen with conjugated base salts of alkali metals in protic solvents;
- by dissolving alkali metals;
- by cathodic generation.

Generation of e_s^- by the electrochemical method, represented by

$$e_C^- \leftrightarrow e_s^-$$

where e_C^- denotes electrons present in the cathode, is of particular interest[30-34]. Generation can be achieved during high cathodic polarisation and should be independent of the electrode material used.

For the cathodic generation of e_s^-, two mechanisms can be distinguished: 'chemical dissolution of electrons' and 'electron thermoemission[35,36]. The former can be compared with an electrochemical process: the electron in the metal is transferred to an acceptor, in this case a cavity. The latter mechanism, introduced by *Brodsky* and *Frumkin*[37], has no electrochemical equivalent: the electrons enter the solution in a delocalized state and are subsequently solvated.

Thermoemission is a well studied process for the metal-vacuum boundary, where it usually proceeds at an appreciable rate only at sufficiently high temperatures. The difference between the energies of the electron in the metal and in solution (*i.e.* the metal-to-solution work function) decreases when a negative potential is applied to the electrode. The work function depends linearly on the electrode potential with a proportionality factor equal to unity. The thermoemission stage determines the kinetics of the generation process, which is described by the *Richardson-Sommerfeld*[22] equation

$$i = A \cdot T^2 \cdot \exp[w_{MS} + \eta \cdot F/R \cdot T]$$

in which: i = the current density ($mA \cdot cm^{-2}$)
$A = 120$ ($A \cdot cm^{-2} \cdot K^{-2}$)
w_{MS} = the metal-to-solution electronic work function at $E = 0$ V (eV)
η = the overpotential (V)
and T, F and R have their usual meaning.

The kinetics described by this equation contrasts with the kinetics of the 'chemical dissolution' process which are described by the standard equation of electrochemical kinetics[38]

$$i = i_0 \cdot \exp[\alpha \cdot \eta \cdot F/R \cdot T]$$

in which:
i_0 = the exchange current density ($mA \cdot cm^{-2}$)
α = the transfer coefficient

The two e_s^- generation mechanisms may be regarded as two parallel and independent processes. Electrochemical dissolution is preferred thermodynamically because the Gibbs free energy of reaction is more negative than for thermoemission. However, for thermoemission, the work function decreases faster with increasing negative potential than the activation energy of dissolution ($\eta \cdot F$ versus $\alpha \cdot \eta \cdot F$). Therefore, at sufficient negative potentials, the thermoemission rate exceeds the electrochemical dissolution rate, and the thermoemission process becomes dominating.

Table I Solvent / electrolyte systems suitable for the electrochemical generation of e_s^-.

solvent	diel. const.	electrolyte	E^0_{0,e_s^-} (V)	Ref.
NH_3	20	all alkali metal salts and NR_4^+ salts	−1.95 vs. NHE	[40]
HMPA[a]	28.7	all alkali metal salts	−3.02 to −3.05 vs. SCE in water	[3]
CH_3NH_2	12.7	Li and Cs salts	−2.9 vs. $Ag/AgNO_3$	[41]
$(H_2NCH_2)_2$	12.9	LiCl, LiI, NaI KI and CsI	−2.57 vs $BBCr^-$[b]	[33]

[a] HMPA = hexamethylphosphoric triamide
[b] $BBCr^-$ = bis(biphenyl) chromium(I)

Because solvent and electrolyte have to be stable under generation conditions, solvents which dissolve alkali metals yielding e_s^- and solvated alkali cations are commonly used. Cathodic generation of e_s^- in general competes with electrolytic deposition of the alkali metal on the electrode. A direct correlation between the ability of a solvent to dissolve alkali metals and the possibility of electrochemical generation of e_s^- in the solution of the metal salts is expressed by the *Makishima* equation[39]. According to this equation it can be stated that the higher the solubility of the alkali metal, the more thermodynamically effective is the cathodic generation of e_s^- compared to alkali metal deposition. Table I contains the solvent/electrolyte systems suitable for the electrochemical generation of e_s^-. In the majority of cases, it is the solvation of the cation that is crucial for the solvent's ability to dissolve alkali metals. Metallic lithium, of which the cation is always more strongly solvated than the cations of other alkali metals, exhibits maximum solubility. So, it is in lithium salt solutions that generation of e_s^- usually takes place. In some cases generation of e_s^- is not observed; this is not unexpected, but it is due to kinetic rather than thermodynamic reasons: the formation of e_s^- is inhibited by the formation of hydroxides and/or other basic compounds of the background salt or by the polymerization of the solvent.

In systems containing tetra alkyl-substituted ammonium salts, e_s^- are found to be chemically stable only when liquid ammonia is used as the solvent. The reason is that the reaction

$$NR_4^+ + e_s^- \rightarrow NR_3 + R^{\cdot}$$

takes place.

There is no clear correlation between macroscopic properties (dielectric constant, boiling point, viscosity, donor or acceptor number) of the solvent and the ability of stabilising electrochemically generated e_s^-.

Solvated electrons can also be generated electrochemically in solvents containing considerable amounts of Brønsted acids[43]. Solvated electrons liberate dihydrogen only very slowly from a whole range of substances containing active hydrogen. This makes it possible to use water and alcohols as H^+ donor for the reduction of organic compounds[44]. To suppress the electrochemical reduction of the protonic compound, metals with a high hydrogen overpotential are used (Hg, amalgams). It was shown that the reversible electron electrode obeys the Nernst equation for a single-charge electron. A reversible electron electrode for liquid ammonia has been known for a long time, see also Ref. 45. In the region of low concentration, an equilibrium has been established for the single-charge electron. At e_s^- concentration higher than 10^{-3} M, associates of the structure $e_s^- M^+ e_s^-$ are formed[46,47]. The

reversible electron electrode can also be realized in solutions of e_s^- in hexamethylphosphoric triamide (HMPA) and others solvents such as 1,3-dioxan-2-one and 3-methyltetrahydrofuran for use in secondary batteries[45].
Using a rotating disk electrode (RDE), the anodic limiting current was determined by diffusion of e_s^- present in the solution, to the electrode[48,49]. By means of a Pt rotating disk electrode, it was found that in a 0.36 M LiCl solution in HMPA, the limiting current density is proportional to the square root of the disc electrode rotation rate, in agreement with the Levich-equation.
Much discrepancy is found on examining the data of various authors concerning e_s^- generation kinetics. According to *Alpatova*[50,51], this can be attributed to the dependence on the state of the surface during e_s^- generation and it was concluded that different results can often be caused by passivation. Ammonia was the solvent for which it was first shown[52] that the properties of e_s^- prepared by different methods were identical. The chief quantitative results of e_s^-, however, have been obtained in HMPA[3,4,53–60]. By means of the rotating-ring-disk electrode, the diffusion coefficient of e_s^- in HMPA could be determined[61].

2.3 Properties of e_s^- in HMPA

When metallic lithium is solvated in HMPA or when HMPA/Li-salt solutions are highly cathodically polarized, the solution turns dark blue. The absorption maximum at 2200 nm is attributed to e_s^-, although the nature of the optical transition is still a subject of discussion. According to a widely accepted model[62], the absorption band conforms to phototransition of an electron from the ground bound 1s state to the excited bound 2p state. An alternative theory[63] is that photoionization occurs, *i.e.* transition of an electron from the 1s level to the delocalized state (*i.e.* the conduction band). The peak energy (0.45 eV), however, is much less than both the ionization energy and the difference in the equilibrium energies of the localized and delocalized states. Consequently, only transition to the bound excited state can take place.
In HMPA solutions of e_s^- and sodium or potassium salts, a peak at 750 nm or at 880 nm is also present. This was attributed to the alkali metal anion[64]. When electrochemical generation of e_s^- is accomplished in HMPA solutions of lithium salts, an EPR signal appears simultaneously. The corresponding g-factor was found to coincide with that of a free electron.

3. The e_s^- as a reducing agent for benzenoid compounds

If we consider the electrochemical reduction of aromatics, it can be postulated that there is no direct transfer of an electron from the cathode to the "sole benzene nucleus[65]. Concerning the reduction of benzene (derivatives) we can distinguish two main pathways:
- direct catalytic hydrogenation and
- reduction by solvated electrons.

3.1 Catalytic hydrogenation

Aromatic rings can be reduced chemically to the fully saturated derivative by direct catalytic hydrogenation[66,67]. High hydrogen pressures and/or high temperatures are often required. As a catalyst, palladium, platinum, PtO, rhodium, and ruthenium are often used. For example, *Dunn* and *Bard*[68] investigated the catalytic activity of platinum black suspensions and a number of supported platinum catalysts for the direct reduction of benzene.

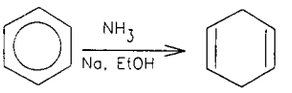


Figure 1. The Birch reduction.

Linear free-energy relationships, involving both steric and electronic parameters have been used successfully in heterogeneous catalysis[69], and the Taft equation has been tested for a set of alkyl substituents[70].
The discovery of the formation of cyclohexene in addition to cyclohexane during the hydrogenation of benzene has led to considerable research efforts being devoted to the development of processes in which high selectivity and yield of cyclic olefins is realized.
In the case of aromatic hydrogenation of substituted benzenes, the major problems are related to controlling hydrogenolysis and/or reduction of other functional groups. Benzyl compounds carrying oxygen or nitrogen functionalities undergo hydrogenolysis readily over Pd, usually with little or no ring reduction[71]. Ring saturation without hydrogenolysis is best accomplished over Ru or Rh and to a lesser extent over Pt. Several workers[72–78] have examined the catalytic hydrogenation of substrates with hydrogen generated electrochemically from an acid solution at a cathode made of the hydrogenation catalyst[66].
In modern technology catalytic hydrogenations are considered to be processes the successful operation of which mainly depends on the proper choice of catalyst. Catalytic hydrogenations are reasonably well understood and the desired activity and chemo-, regio-, and sometimes even stereoselectivity can be achieved by an appropriate choice of catalyst and reaction conditions.

3.2 Reduction by solvated electrons

3.2.1 Dissolving metal reductions When aromatics are reduced by sodium (or potassium or lithium) in liquid ammonia (such reductions are known as 'dissolving metal reductions') in the presence of an alcohol, |1,4| addition of hydrogen takes place and nonconjugated cyclohexadienes are produced. This reaction, known as the Birch reduction[79,80], is shown in Figure 1. A mechanism, proposed in 1959 by *Krapcho* and *Bothner-By*[81], is given in Figure 2. The reducing species is the solvated electron (e_s^-), chemically generated by the ionisation of sodium in ammonia. In the first step a reversible electron addition takes place forming a radical anion, followed by the rate determining step (rds), which is the addition of the first proton. A second electron addition and a second protonation yields the product.
The competition between the formation of 1,3-cyclohexadiene and 1,4-cyclohexadiene has been examined[82]. The former is usually regarded as a "thermodynamic" product and the latter as a "kinetic" product.

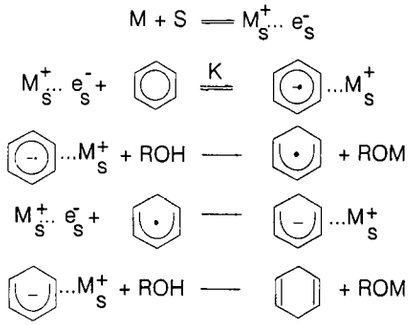


Figure 2. Proposed mechanism for the chemical reduction of benzene.

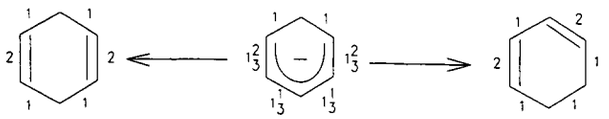


Figure 3. Hine's *'Principle of least motion'.*

Experimentally, the second protonation step has been shown to occur predominantly *para* to the first protonation. Different explanations have been given for this observation. Charge density has been considered an important feature of this process with the notion that protonation should occur at the site of greatest negative charge. *Ab initio* molecular orbital calculations have been carried out to examine the benzene radical anion[83,84], the cyclohexadienyl radical[85], the cyclohexadienyl anion[86], and cyclohexadiene[87]. Molecular electrostatic potential plots of (substituted) cyclohexadienyl anions predict that "kinetic" protonation takes place preferentially at the carbon atom *para* to the first protonation site. This is so regardless of substituent or substituent position. Also the Pople method indicates greatest charge density at the *para* position[88,89]. *Hine*[90,91] suggested that the protonation at the *para* position illustrates the operation of the "principle of least motion". According to this principle,

> *"... those elementary reactions will be favoured that involve the least change in atomic position and electronic configuration..."*

The principle can be illustrated in the following manner: the valence-bond bond orders for the six carbon-carbon bonds (on the assumption that each of the three forms contributes equally) of the cyclohexadienyl anion are (going around the ring) $\frac{5}{3}$, 1, 1, $\frac{5}{3}$, $\frac{4}{3}$, and $\frac{4}{3}$.
When the carbanion is converted to the 1,4-diene, the change is as pictured in Figure 3. It can be seen that the two bonds whose bond order is 1 are unchanged in the two products, but for the other four bonds there is a change. If the 1,4-diene is formed, the change is $\frac{1}{3} + \frac{1}{3} + \frac{1}{3} + \frac{1}{3}$, while formation of the 1,3-diene requires a change of $\frac{1}{3} + \frac{2}{3} + \frac{2}{3} + \frac{1}{3}$. Since a greater change is required to form the 1,3-diene, the principle of least motion predicts formation of the 1,4-diene[92]. It was found that the 6-position of the carbanion, shown in Figure 4, has a somewhat greater electron density than the 2-position, which presumably would make the former more attractive to a proton[93].
It was stated[82] that dienes can undergo proton abstraction when amide ions are present, and create an equilibrium such as illustrated in Figure 5.
When an alcohol is used as proton donor, conjugated products are generally not observed since alkoxides will not lead to deprotonation of the product. The presence of a strong base (*e.g.* an alkali amide) can provide the equilibrium conditions and the reduction reaction may

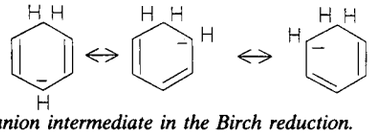


Figure 4. Carbanion intermediate in the Birch reduction.

Figure 5. Possible equilibrium conditions during metal-ammonia reductions.

become quite sensitive to the alkali metal. It is also possible that the 1,3-cyclohexadiene formed is reduced further under the reaction conditions and the final product will be cyclohexene.
Reactions for some substituents follow a course different from that of the normal Birch reduction. For example, groups such as NO_2 and CN are reduced preferentially to the ring. It is possible to reduce the benzene ring without reducing the substituent, but special conditions or treatments are then required. For example, benzonitriles, benzamides[94], sodium benzoates and aromatic carboxylic esters[95] were reduced to give the 1,4-dihydro derivatives. By definition a Birch reduction is one in which the alkali metal is added to a well-stirred mixture of the substrate, alcohol and ammonia. The method is predominantly applicable to simple aromatic compounds. Modifications are methods introduced by *Nelson* and *Wilds*[96] (use of an auxiliary solvent, lithium instead of sodium), *Johnson*[97] (excess of alcohol) and *Dryden*[98] (redistilled ammonia). Aromatic reduction by solutions of lithium in low molecular amines (the Benkeser reduction) gives more extensively reduced products[99–103]. The lithium/1,2-diamino ethane system[104,105] is more powerful. Thus, treatment of benzene with an excess of sodium in ethanol and ammonia affords 1,4-cyclohexadiene[106], reduction by Li/methylamine affords cyclohexene with some cyclohexane, and in Li/1,2-diamino ethane the reduction gives a mixture of cyclohexene and cyclohexane.

3.2.2 Electrochemical reductions The electrochemical alternative of the Birch reduction was first shown by *Birch* himself[107], reducing 1-methoxy-3-methyl benzene to the corresponding 1,4-dihydro-derivative; the reaction was carried out at a smooth copper cathode with a current density of 0.04 $A \cdot cm^{-2}$ in a saturated solution of sodium ethoxide in liquid ammonia containing ethanol. Here again e_s^-, this time generated electrochemically by high cathodic polarisation, are the predominant reducing species and this leads to the Birch reduction of several aromatics[108–110].
Benkeser and coworkers[111,112] showed that benzene could be reduced in a solution of lithium chloride in methylamine. An electrochemical cell with and without an asbestos divider was used and gave cyclohexene and 1,4-cyclohexadiene, respectively, see Figure 6. It was proposed that in the former the lithium amide formed leads to reversible Birch conditions and provides the equilibrium between 1,4- and 1,3-cyclohexadiene, while in the latter lithium amide is neutralized by methylamine hydrochloride which is formed at the anode. The mechanism of the reaction is pictured in Figure 7.
Nonconjugated aromatic olefins (terminal or internal) with the double bond at least two carbons removed from conjugation, were also reduced selectively to give 2,5-dihydro-aromatic olefins as the major product[113]. Methylamine was also used as a solvent in the electrochemical reduction of 5-sterone methyl ether giving 1,4-dihydro-3,17b-5-stradiol 3-methyl ether[114] and in the reduction of substituted benzylamines[115].
In 1,2-diamino ethane saturated with LiCl, benzene was reduced to give cyclohexene with a trace of cyclohexadiene and no detectable cyclohexane[116].
Aromatic reduction by electrochemically generated e_s^- was also achieved in ethanol/HMPA mixtures containing

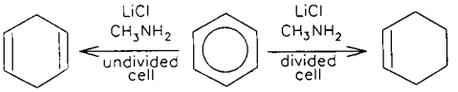


Figure 6. The electrochemical Benkeser reduction.

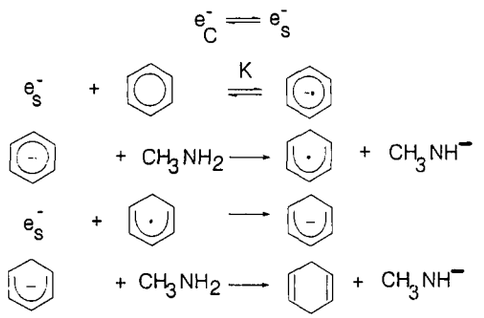


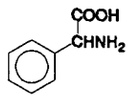
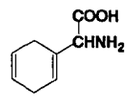
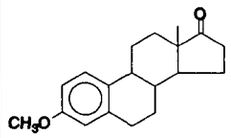
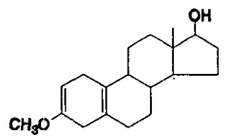
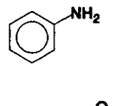
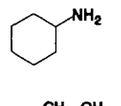
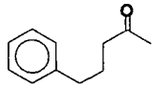
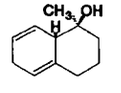
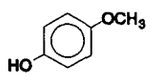
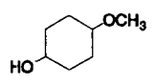
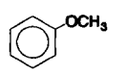
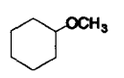
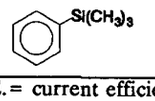
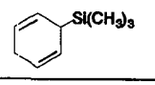
Figure 7. Proposed mechanism for the electrochemical reduction of benzene in a LiCl / methylamine solution.

LiCl[117–122]. Ferrocene can also be synthesized, as well as tetralines, starting from naphthalene[123, 124].
In most cases, the fully saturated derivative was obtained. In the case of benzene reduction, the relative amounts of cyclohexadiene, cyclohexene and cyclohexane were found to depend on the concentration of ethanol, the current density and the temperature of the reaction[125]. The influence of water on the reduction of benzene in HMPA was studied using a rotating ring-disk electrode[126].
Foise and coworkers[127] demonstrated that direct catalytic hydrogenation of benzene could be combined with the reduction by e_s^-. Pt and Ru colloidal particles were prepared and dispersed in a HMPA/ethanol solution and hydrogen gas was supplied up to 10 psig. Addition of Ru particles resulted in a significant increase in the percentage of reduced benzene.
It has been shown that reactions similar to those of the alkali-metal/ammonia type can be performed in water[128] or in mixed aqueous organic media[129–135] containing tetraalkylammonium salts as electrolytes and using mercury as the cathode. It has been suggested[136–138] that NR_4^+ ions are reduced on mercury to form materials dubbed "amalgams". It seems that these "amalgams" are directly involved as a catalyst. Table II shows some examples of aromatic reductions by electrochemically generated e_s^-.
The electroreductive cyclization, presented by *Shono*[140], requires special attention; β- or γ-aryl ketones can be converted to cyclic tertiary alcohols by an electroreductively induced intramolecular addition of the carbonyl group to the aromatic ring. The product seemed to be practically a single stereoisomer. Another interesting application is the reduction of fullerene C_{60} in liquid ammonia[141].

4. Concluding remarks

Thanks to research all over the world, we now have a better knowledge of electrochemical aspects and synthetic possibilities of solvated electrons (e_s^-).
In this paper, some examples have been given of the reduction of benzenoic compounds by means of e_s^-, generated chemically or electrochemically. It has been shown that high selectivity for the production of olefinic products can be achieved.
Solvated electrons as reducing agents have found, so far, limited application in the field of organic synthesis. Inconveniences such as having to deal with alkali metals, and therefore strongly basic conditions, and high sensitivity towards the presence of water may be mentioned as possible causes.

Table II Aromatic reduction reactions by electrochemically generated e_s^-.

starting material	product	system	yield (%) [C.E.[a] (%)]	ref.
		Pt NH_3/LiOAc H_2O/*t*BuOH	72 [45]	[119]
		Pt CH_3NH_2/LiCl	93 [44]	[113]
		Al HMPA/LiCl EtOH	43.8-48 [41.2-45.6]	[120]
		Sn ^{i}PrOH/Et_4N-OTs[b]	70	[140]
		Al HMPA/LiCl EtOH	34.3-37.2 [32.5-35.2]	[121]
		Al HMPA/LiCl EtOH	45.8	[118]
		undivided cell CH_3NH_2/LiCl ^{i}PrOH	31	[139]

[a] C.E. = current efficiency
[b] Ts = p-toluene sulfonate

Electrochemical generation of e_s^- may remove some of these inconveniences, although rather extreme reaction conditions are in most cases inevitable.

However, electrochemical generation of e_s^- offers some advantages. It enables control of the current density, and therefore the reducing agent supply. High current densities can be reached because of the relatively high diffusion coefficient of e_s^-, and in some cases, product selectivity can be achieved by using a divided or an undivided electrochemical cell.

In order to enlarge the industrial application for e_s^- as reducing agents, more emphasis should perhaps be placed on the development of processes in aqueous media.

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