The Reduction of Organic Compounds by Solvated Electrons Generated Electrochemically

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The present review deals with the reduction of organic compounds by solvated electrons generated at a cathode. The general conditions necessary for the electrochemical production of solvated electrons, and the systems in which this process is possible, have been examined. The characteristic features of the reactions of organic compounds with solvated electrons compared with other methods of reduction have been discussed.

Specific data on the reduction by solvated electrons of individual classes of substances difficult to reduce, aromatic and unsaturated compounds, ketones, and derivatives of carboxylic acids—amides, nitriles, and esters—have been examined. The review will be useful for specialists in the physical chemistry of solvated electrons, theoretical electrochemistry, the electrochemistry of organic compounds, and organic synthesis.

The bibliography contains 92 references.

CONTENTS

I. INTRODUCTION

Among the varied methods for the electrochemical synthesis of organic compounds, reduction by solvated electrons generated at a cathode has found application in recent years.

Solvated electrons in the liquid phase can be obtained by various methods, chiefly radiation-chemical, photochemical, and photoelectrochemical methods, via atomic or molecular hydrogen, by dissolving alkali metals, and by cathodic generation. Not all of these methods, however, are suitable for the preparative reduction of organic compounds. The most universal method of obtaining solvated electrons is the radiation-chemical method. In systems based on the most varied solvents,[1] solvated electrons are obtained by the removal of electrons from molecules, ions, or atoms by the action of X-rays or gamma-radiation, and also fast electrons. In photochemical generation, solvated electrons are produced by the action of light on substances which are electron donors.

These two methods, however, in addition to solvated electrons, produce radicals and ions which react rapidly with electrons, and this makes it difficult to use these methods of generation for the preparative reduction of organic compounds. Unstable systems are also produced when the electrons are obtained by photoelectrochemical methods.[2]

When a mixture of molecular and atomic hydrogen is passed through aqueous alkali solutions with pH > 12, hydrated electrons (e_h^-) are formed:[3-5]

$$H + OH^- \rightarrow e_h^- \ .$$
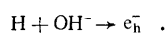
In liquid ammonia, molecular hydrogen reacts with the amides anion:

$$^{1}/_{2}H_2 + NH_3^- \rightleftharpoons e_s^-$$
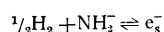
where e_s^- is the solvated electron. The process takes place at high pressures of hydrogen and high concentrations of potassium amide.[5-8] The reactions with hydrogen have a restricted range of application, however, since they are known only for water and ammonia, and require complex apparatus.

For the reduction of organic compounds by solvated electrons, it is more convenient to use the solution of alkali metals and electrochemical generation. These methods make it possible to produce systems in which the solvated electrons are stable. In many cases, electrolysis makes it possible to control the concentration of electrons and to carry out a process repeatedly. The use of cathodic generation makes it possible to avoid dangerous operations with alkali metals. The main limitations of generation are associated firstly with the use of a conducting medium, that is the use of electrolytes and a solvent with a fairly high dissociating power, and secondly with the need to work in a medium stable to cathodic reduction.

II. SYSTEMS FOR GENERATING SOLVATED ELECTRONS ELECTROCHEMICALLY

The electrochemical generation of solvated electrons takes place at very negative potentials. Table 1 compares the values of the standard equilibrium potential of the electron electrode with the corresponding values for other electrodes. The term "electron electrode" is used to describe an inert metallic electrode in which the electrons (e_m^-) are in equilibrium with solvated electrons in a solution.

Table 1. Standard equilibrium potentials (ϕ_0, V).[9]

$e_s^- \rightleftharpoons e_m^-$	$Na \rightleftharpoons Na^+ + e_m^-$	$K \rightleftharpoons e_m^- + K^+$	$Rb \rightleftharpoons Rb^+ + e_m^-$	$Cs \rightleftharpoons Cs^+ + e_m^-$	$Li \rightleftharpoons Li^+ + e_m^-$
Water (n.h.e. in water, 25 °C)					
−2.77−−2.88	−2.714	−2.924	−2.925	−2.923	−3.045
Ammonia (n.h.e. in ammonia, 25 °C)					
−1.95	−1.89	−2.04	−2.06	−2.08	−2.34
HMPA (s.c.e. in water, 5.5 °C)					
−3.02−−3.05	−2.92	−3.04	−3.00	−2.96	−3.21

Note: n.h.e. = normal hydrogen electrode; s.c.e. = saturated calomel electrode.

The data in Table 1 show firstly that the potentials of the electron electrode are close to the potentials of the alkali metals, that is the reducing power of solvated electrons is comparable with that of the strongest reducing agents known at present.

In the case of liquid ammonia, the decrease in the difference in the standard potentials of the electron and hydrogen electrodes is due to the higher energy of formation of the ammonium ion from the hydrogen ion, compared with the energy of formation of the hydroxonium ion in water. Secondly, the cathodic generation of electrons can be carried out only in systems in which neither the solvent nor the background salts undergo direct reduction at very negative potentials. In spite of the severity of this requirement, the electrochemical generation of solvated electrons can be carried out in a whole range of systems, which are classified in Table 2.

Table 2. Classification of systems suitable for the cathodic generation of solvated electrons.[10]

A Solvated electrons stable		B Solvated electrons unstable	
A-2	A-2	B-1	B-2
Liquid ammonia, HMPA Li^+, Na^+, K^+, Rb^+, Cs^+	methylamine, glyme* diglyme**, ethylenediamine, Li^+, Rb^+, Cs^+	HMPA, dimethyl, sulphoxide, diglyme, $NAlk_4^+$	HMPA-water (alcohol), diglyme-water, $NAlk_4^+$

* Glyme = 1, 2-dimethoxyethane; ** diglyme = dimethyl ether of diethyleneglycol.

The cathodic generation of electrons is most frequently carried out using systems in which the solvated electrons are chemically stable. These are the systems in liquid ammonia, hexamethylphosphortriamide (HMPA), amines, and ethers (group A). The counter-ions in the systems of this group are generally alkali metal cations, although in liquid ammonia at low temperatures it is possible to use salts of aluminium, magnesium, the tetra-substituted ammonium ion, etc. In the systems of sub-group A-1, it is thermodynamically more favourable for the cathodic generation of solvated electrons to take place on solid electrodes, that is for an electron to be removed from the metal into the solution, $e_m^- \rightarrow e_s^-$, and not the deposition of the alkali metal, $M^+ + e_m^- \rightarrow M$. For the same reason, the reaction in the volume involving the reduction of the cations of the background by solvated electrons, $M^+ + e_s^- \rightarrow M$, does not take place. Table 1 shows that for liquid ammonia and HMPA, the standard equilibrium potential of the electron electrode is more positive than the potential of the lithium electrode, and is close to the potentials of the other alkali metals. Under real cathodic generation conditions, dilute ($10^{-5}-10^{-2}$ M) solutions of solvated electrons are formed, displacing the equilibrium potential of the electron electrode by 0.1–0.3 V to more positive values. In the case of HMPA, the binding of electrons by the cations of all alkali metals except lithium to form stable non-paramagentic associates $M^+..2e^-$ acts in the same direction.[10] The ratio of the potentials expected from this indicates that generation is thermodynamically preferred to the deposition of the alkali metal.

In the systems of sub-group A-2, the reactions involving reduction are not thermodynamically unfavourable for all alkali metal cations. Electrolytic deposition of the metal

generally takes place in sodium salt solutions, and cathodic generation of electrons in solutions of lithium, rubidium, and caesium salts. Systems containing potassium salts occupy an intermediate position.

All the solvents of group A are thermodynamically unstable to the action of high cathodic potentials and solvated electrons. In these systems, however, the reduction of the solvent at the electrode and the chemical reaction of the solvent with solvated electrons in the volume are kinetically hindered (see below).

The systems of group B include solutions of tetra-alkylammonium salts (mainly tetrabutylammonium salts) in aprotic solvents (sub-group B-1) or mixtures of an aprotic and a protonic solvent (sub-group B-2). In these systems there is kinetic retardation of the cathodic reduction of the components of the solution at the electrode, whereas the chemical reaction of the electrochemically generated electrons with some component of the solution takes place relatively rapidly. The electrons disappear by reacting with the cations of the salt or the molecules of the solvent.

It can be seen from Table 2 that the question of the participation of solvated electrons in reduction processes can be raised not only when liquid ammonia and similar solvents are used, but also in systems with an appreciable concentration of proton donors.

Table 3. Physical properties of the solvents.[10]

Solvent	M.p., °C	B.p., °C	E (T, °C)	η, cP (T, °C)	DN	AN
Ammonia	—77.7	—33.4	20.0 (—34)	0.2558 (—34)	59.0	—
Methylamine	—92.5	—6.7	12.7 (—22.8)	0.353 (—22.8)	--	—
Ethylamine	—81.0	16.6	5.9 (20)	—	55.5	—
Ethylenediamine	11.0	116.5	12.9 (25)	1.54 (25)	55.0	—
Tetrahydrofuran	—65.0	64—65	7.4 (25)	0.764 (25)	20.0	8.0
HMPA	7.2	232	29.0 (25)	3.1 (25)	38.8	10.6
Thiohexamethyl-phosphortriamide	29.0	94 (130 H/м²)	39.5 (30)	5.55 (30)	—	—
Glyme	—58.0	82—85	7.2 (25)	0.455 (25)	24.0	10.2
Diglyme	—	161—163	7.2 (25)	2.0 (20)	—	10.2
Water	0	100	78.5 (25)	1.01 (20)	18.0 (33)	54.8
Ethanol	—114.5	78.3	24.3 —	1.08 —	—	37.1
Methanol	—97.5	64.5	32.6 —	0.55 —	19.0	41.3

Note: E = dielectric constant; η = viscosity; DN = donor number; AN = acceptor number.

The suitability of the systems given in Table 2 for the reduction of organic compounds by solvated electrons generated at a cathode is determined chiefly by the ratio of the rates of the reactions of the electrons with the organic compound and with the components of the solution. All the systems of group A are obviously suitable for this purpose. Table 3 gives various physicochemical characteristics of the solvents listed in Table 2. The combination of medium dielectric constant values with high donor numbers ensures that liquid ammonia and HMPA bring about effective dissociation of the background salts and hence effective conductivity of the solution (reaching $10^{-3}-10^{-2}$ $\Omega^{-1}cm^{-1}$). Another advantage of liquid ammonia is its ease of purification. The use of this solvent, however, requires increased pressure or reduced temperature. The high boiling point of HMPA makes it possible to use it under ordinary conditions, but the purification of HMPA is very laborious,[11] and the toxicity of this solvent makes it necessary to take special precautions when working with its solutions.[10,12,13]

Of the systems of sub-group B, only the solutions in
dimethyl sulphoxide are unsuitable for electrosynthesis using
solvated electrons, since dimethyl sulphoxide is an effective
acceptor of solvated electrons.[1]

It is important to note that solvated electrons can be
generated in mixtures containing considerable quantities of a
proton donor, that is essentially in mixed solvents.[14]
Solvation in these systems should be heteroselective in
character; cations are solvated by the aprotic component,
and anions by the protonic component. This ensures the
solution and dissociation of the background salts. The
solvating power of the protonic component also extends to
the solvated electron. Clearly defined heteroselective
solvation, for example in mixtures of HMPA with water or
alcohol, should lead to an increase in the thermodynamic
probability of the cathodic generation of electrons. The
strong solvation of cations by HMPA hinders the reduction of
the cation of the background salt competing with generation,
and strong solvation of the electrons by the protonic solvent
ensures the electrochemical generation of electrons.

The cathodic reduction of water and aliphatic alcohols in
aprotic solvents is usually difficult, even on platinum.
Fig.1 gives the cyclic voltammetric curves in a solution of
lithium chloride in mixtures of HMPA and ethanol.[15] The
increase in the current strength at higher absolute values of
the negative potentials corresponds to the generation of
solvated electrons. The peak corresponding to the cathodic
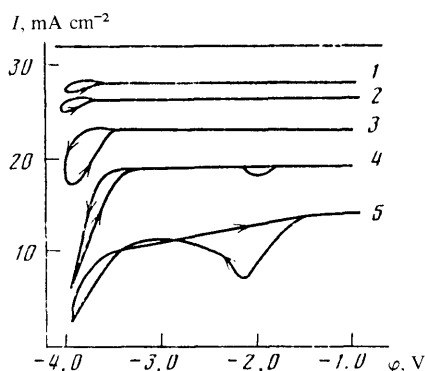reduction of alcohol appears only at a concentration of
50 mole %.

Fig.2 gives the cathodic polarisation curves recorded in
mixtures of two parts by volume of HMPA with one part by
volume of water or ethanol, corresponding to concentrations
of the aprotic component of 17 mole % and 42 mole % respec-
tively. According to spectral data,[16] this composition of the
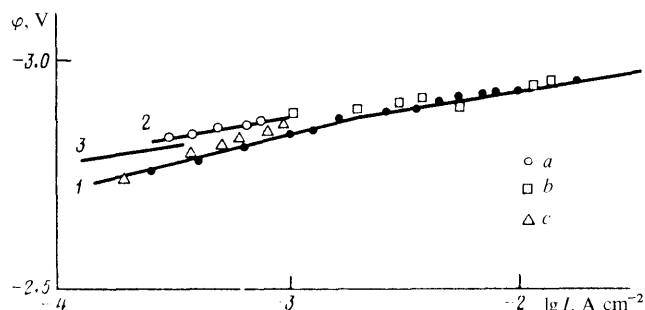mixture with water still ensures the preferential solvation of
the electron by water.

Figure 2. Dependence of the potential ϕ, V (s.c.e.) on the
current density (I, A cm^{-2}) in tetrabutylammonium tetra-
fluoroborate solutions (0.1 M) at 25 °C; 1) amalgamated
copper (a, b) in a mixture of HMPA with water (a) and with
ethanol (b), and mercury in a mixture of HMPA with water
(c); 2) mercury in hexamethylphosphortriamide; 3) copper
in HMPA.[14]

Figure 1. Cyclic voltammetric curve (3.3 mV s^{-1}) for a
platinum electrode in a solution of lithium chloride (0.5 M) in
a mixture of HMPA and ethanol; alcohol concentration (mole %):
1) 0; 2) 14; 3) 35; 4) 50; 5) 67;[15] (Ag/0.1 M Ag$^+$).

To suppress more reliably the electrode reduction of the
protonic component, it is necessary to use metals with a high
hydrogen overvoltage (mercury, amalgams), and also to use
a tetrabutylammonium salt as background. These salts not
only are the most difficult to discharge with the formation of
amalgams, but also decrease sharply the rate of the cathodic
discharge of water. The retardation can be attributed to
the ease of adsorption of the cation on mercury, leading to
shielding of the surface, and to a decrease in the concentra-
tion of water in the layer next to the electrode as a result of
the preferential solvation of the tetrabutylammonium cations
by the organic component of the mixed solvent.

Curve 1 in Fig.2 shows that the cathodic process in the
mixtures takes place at very negative potentials. The
potentials in all the systems were measured relative to the
saturated calomel electrode in water. The ethanol/water and
HMPA/water interphase potential jumps are 30 mV and 150 mV
respectively.[17] The interphase potential jumps between
water and the systems being studied probably do not exceed
100–150 mV, and this should not introduce qualitative
changes in the observed picture. The cathodic process
described by curve 1 may correspond to several reactions:
the discharge of a proton donor, the discharge of the tetra-
butylammonium cation with the formation of an amalgam, and
the electrochemical generation of electrons. The first
suggestion is not consistent with the similarity in the poten-
tials for the mixtures with water and with alcohol (curves 1a
and 1b). Moreover, the potentials of curve 2, recorded in
HMPA without water or alcohol, are close to the potentials in
mixtures containing a proton donor. Curve 3, which cor-
responds to the cathodic process at a copper electrode in
HMPA, practically coincides with the curve for a mercury
electrode, making it possible to reject the suggestion that the
cation is discharged and to assume that the cathodic process
is the electrochemical generation of solvated electrons.

The possibility of using protonic media for the reduction of
organic compounds by solvated electrons is closely related to
the high selectivity of the reactions of solvated electrons. In
addition to the reduction of compounds difficult to reduce,
solvated electrons liberate hydrogen only very slowly from a
whole range of substances containing active hydrogen. It is
the low rate of reduction of water and aliphatic alcohols by
solvated electrons that makes it possible to use them as proton
donors for the reduction of organic compounds. Water in
solutions of sodium and lithium perchlorates in HMPA does not

react with solvated electrons up to a water concentration of 0.1 M.[18]   Table 4 gives the rate constants for the reactions of solvated electrons with water and alcohols in various media.

Table 4.   Rate constants (k) for the reactions of solvated electrons with water and alcohols.

Solvent	Electron acceptor	k, litre mole^{-1}s^{-1}	Refs.
Water	H_2O	16	[1]
Ethanol	C_2H_5OH	$4.7 \cdot 10^3$	[19]
Ethylenediamine	H_2O	24.7	[20]
Heavy water	D_2O	1.25	[1]
Water	CH_3OH	$\leqslant 1 \cdot 10^3$	[21]
Water	C_2H_5OH	20	[21]

III. THE REACTIONS OF SOLVATED ELECTRONS WITH THE SOLVENT

The reactions of solvated electrons with organic compounds take place in parallel with their reactions with the molecules of the solvent.   All the systems in which solvated electrons are fairly stable are metastable, and gradually decompose as a result of the chemical reaction of the solvated electrons with the solvent.   This reaction is generally catalytic, and its rate is increased by impurities, the walls of the apparatus, and reaction products, so that its quantitative study is difficult. There are few published data on this topic.   The addition of two electrons to the HMPA molecule gives the dimethylamide anion and the diamidophosphite anion:[22]

$$[(CH_3)_2N]_3PO + 2e_s^- \rightarrow (CH_3)_2N^- + [(CH_3)_2N]_2PO^- \ .$$
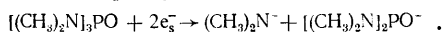
In highly purified solutions, it is this reaction that determines the stability of the solvated electrons.   The time taken for the disappearance of the colour of a 10^{-2} M solution of electrons in a background of sodium perchlorate in HMPA was 4 h at 25 °C and 24 h at 5 °C.[23]

In very pure solutions in liquid ammonia, the reaction is slow, particularly at temperatures of -33 °C and below.

$$NH_3 + e_s^- \rightarrow NH_2^- + {}^1/_2H_2 \ .$$

The rate of the reaction is increased with increase in temperature and under the influence of catalysts.   The catalysts include platinum black, iron oxides, the walls of the cell, and the products of the reaction of the electrons with impurities.   The reaction of solvated electons with liquid ammonia may be more closely related to the reduction of an organic compound.   Thus in the reduction of ethylene oxide in liquid ammonia by solvated electrons obtained by dissolving alkaline earth metals, the amide alkoxide, for example $NH_2CaOC_2H_5$, is formed.[24]

The reduction of tetrahydrofuran by solvated electrons generated at a cathode in HMPA has been studied.[15]   The ether is not reduced in the absence of a proton donor.   At an ethanol concentration of 50 mole %, tetrahydrofuran is converted into a mixture of n-C_4H_9OH, n-$C_4H_9OC_2H_5$, and n-C_4H_{10}.   In the reduction of ethers with one aromatic group, hydrogenation of the ring takes place first.   Thus in a mixture of ethanol (67 mole %) with HMPA in a background of lithium chloride, anisole is reduced to methoxycyclohexane.[25]

The possibility that ethers may be reduced in the presence of impurities which are proton donors must be taken into account when they are used for the cathodic generation of electrons.

IV. THE CHARACTERISTIC FEATURES OF THE REDUCTION OF ORGANIC SUBSTANCES BY SOLVATED ELECTRONS GENERATED AT A CATHODE

Solvated electrons have exceptionally powerful reducing properties.   Their electrochemical generation requires high negative potentials, so that solvated electrons cannot be generated in the presence of substances which are easily reduced.   It is therefore appropriate to use solvated electrons to reduce substances whose reduction requires fairly high potentials.

The reduction of organic compounds by solvated electrons generated at a cathode is usually carried out in systems in which the solvated electrons are stable.   Substances which dissolve alkali metals to give solvated M^+ cations and electrons are used for this purpose:
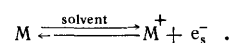
$$M \xrightarrow[\ \ \ \ \ ]{\text{solvent}} M^+ + e_s^- \ .$$

Table 5.   The solubility of alkali metals and the possibility of the cathodic generation of solvated electrons in various media.[10]

Solvent	Solubility of alkali metals	Cathodic processes in solutions of salts of the corresponding metals
Liquid ammonia	all alkali metals readily soluble (more than 10 mole per 1000 g solvent)	cathodic generation of electrons in solutions of all alkali metal salts
Methylamine	[Li] = 7.4 M* [Na] = 4 × 10^{-3} M [K] = 10^{-2} M Cs—soluble	salts: Li—generation of electrons Na—metal deposition K—generation + deposition Cs—generation of electrons
Ethylamine	Li—soluble	Li salts—generation of electrons
Glyme	Li Na } insoluble K Rb } soluble Cs	salts: Li Na metal deposition K Rb generation of electrons Cs
HMPA	all alkali metals readily soluble	NaClO$_4$ + 18-crown-6 in solutions of salts of all alkali metals—cathodic generation of electrons
Thiohexamethyl-phosphortriamide	Na—insoluble	Na salts—metal deposition

*−23 °C.

The relationship between the solubility of an alkali metal in a given solvent and the thermodynamic possibility of carrying out the cathodic generation of electrons in it is given by Makishima's equation:[26]

$$\varphi^0_{M/M^+} - \varphi^0_{e_s^-} = -\frac{RT}{F} \ln a_{M^+} a_{e_s^-}$$

where φ^0_{M/M^+} is the standard potential of the alkali metal; $\varphi^0_{e_s^-}$ the standard potential of the electron electrode; and a_{M^+} and $a_{e_s^-}$ the corresponding activities in a solution saturated with the alkali metal.   Makishima's equation shows that the higher the solubility of the alkali metal, the greater the difference in the standard potentials, that is the more thermodynamically favourable the cathodic generation relative to the electrodeposition of the alkali metal, which is the main reaction competing with the generation of electrons.   The quantitative application of the equation is difficult, since usually only the total solubilities of the alkali metals in different media are

known, but it provides a good qualitative explanation of the observed regularities illustrated in Table 5.

Comparison of the data in Tables 3 and 5 shows that there is no correlation between the physical properties of the solvents on the one hand and their ability to dissolve alkali metals and the possibility of electrochemical generation of solvated electrons on the other. Thus for example on going from HMPA to thiohexamethylphosphortriamide (on replacing oxygen by sulphur), the dielectric constant and the dipole moment increase. At the same time, however, the medium loses its ability to dissolve alkali metals and hence the possibility of the electrochemical generation of solvated electrons; this can be related to the decrease in the solvation of the alkali metal ions on going to the thio-derivative. Although the solvating power of the medium both with respect to the cation and with respect to the electron should have a decisive influence on the solution of alkali metals and the cathodic generation of electrons, the main influence is usually shown by the solvation of the cations. Tables 3 and 5 show that liquid ammonia and HMPA, which dissolve alkali metals most readily, have high donor numbers, which are combined with relatively high dielectric constant values. Increase in the energy of solvation of the cations displaces the equilibrium potential of an alkali metal in a solution of its own cations to more negative values, and hence increases the thermodynamic probability of the cathodic generation of solvated electrons. This is facilitated both by the use of solvents with high donor numbers and by binding the cations with special complex-forming reagents, cryptates and crown ethers. Complex formation in this way facilitates generation in systems in which the alkali metal is deposited in the absence of the additive (Table 5).

When an organic substance is added to a system in which cathodic generation of solvated electrons can take place, in the general case the stationary polarisation curves show the formation in this way facilitates generation in systems in which are not too negative, direct reduction of the organic compound at the electrode will take place. Under certain conditions, retardation of this process takes place, displacing the potential sharply towards negative values, due to the start of generation (see Fig.6 below). The limiting current of the electrode reduction of an organic compound may be a diffusion current (supply of the organic substance) or a passivation current (change in the state of the electrode surface as a result of the formation of tarry products by the organic compounds or films of the hydroxides of the cations of the background salts). At the generation potentials, the additive is reduced by two parallel routes: directly at the electrode at a rate corresponding to the limiting current, and as a result of chemical reaction with the solvated electrons. The rate of the direct reduction in the generation range is independent of the potential. With increase in the generation current, the proportion of direct reduction decreases. For many organic compounds, the electrode reduction is hindered for kinetic reasons, and most of the substance is reduced by reaction with solvated electrons.

One of the advantages of the reduction of organic compounds by electrons obtained electrochemically is the possibility of using higher current densities than in direct cathodic reduction. This is due firstly to the high value of the diffusion coefficient of solvated electrons. The corresponding values for water, ammonia, and HMPA are given in Table 6. Solvated electrons are several times more mobile than common ions (the mechanism of the motion is similar to Grotthus' relay mobility). It should be noted that the Walden product (the product of the diffusion coefficient and the viscosity of the solvent) is approximately the same for the three solvents. This feature can be used to estimate the values for solvents with unknown solvated electron mobilities.

A second feature ensuring the rapid removal of solvated electrons from the electrode is intensive convection due to the decrease in the density of the solution at the cathode surface. This phenomenon is related to the increase in the volume of the solution when electrons are introduced into it. In contrast to the electrostriction accompanying the solvation of ordinary ions, the formation of solvated electrons gives an increase in volume of $65-95$ ml mole^{-1} for liquid ammonia[5] and ~80 ml mole^{-1} for HMPA.[32] The current densities of the generation of solvated electrons may be 2500 or more time the diffusion currents of organic compounds to the electrode, as demonstrated[33] for the reduction of anthracene.

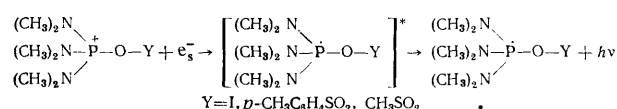**Table 6.** Diffusion coefficients (D, cm^{2}s^{-1}) of solvated electrons in liquid ammonia, water, and HMPA.

Solvent	T, °C	Method of determination	$10^4 D$, cm^{2}s^{-1}	$10^5 D \cdot \eta$, cm^{2}cP s^{-1}	D/D_{Na^+}	Refs.
Liquid ammonia	−36.0	chronopotentiometric anodic oxidation of electrons	1.45	—	—	[27]
		measurement of electrical conductivity and transport numbers	1.74	4.45	6.7	[28,29]
Water	room temp.	radiation-chemical method, measurement of electrical conductivity	0.49	4.90	3.7	[21]
Hexamethyl-phosphortriamide	room temp.	radiation-chemical method, current relaxation curves	0.14	4.59	10.0	[30,31]

A characteristic feature of the reaction of solvated electrons with organic substances is chemiluminescence. The luminescence is produced simultaneously with the cathodic generation of the solvated electrons, and may be very intense.

One group of reactions accompanied by chemiluminescence consists of the reactions of solvated electrons with organic cations and radical-cations to give neutral molecules or radicals.

Thus cyclic voltammetry with simultaneous recording of the luminescence spectra showed that N,N,N',N'-tetramethyl-para-phenylenediamine does not undergo direct cathodic reduction in a solution of sodium perchlorate in HMPA, but can be oxidised reversibly to a radical-cation which reacts with solvated electrons to give an excited molecule of N,N,N',N'-tetramethyl-para-phenylenediamine, which returns to the ground state with the emission of a quantum of light.[34,35] Similar results were obtained[36] with N,N,N',N'-tetramethylbenzidine, N,N-dimethylanisidine, and other amine derivatives which form stable radical-cations.

Luminescence was also observed[37] when thoroughly purified solutions of salts of various alkali metals in HMPA were electrolysed under galvanostatic pulse conditions without separating the cathode and anode compartments. It was suggested that the chemiluminescence is due to the reaction of the solvated electrons with a pseudo-phosphonium cation, which gives a neutral radical in an excited state; this radical returns to the ground state with the emission of a quantum of light:

$$
\begin{array}{l}
(CH_3)_2N \\
(CH_3)_2N-\overset{+}{P}-O-Y + e_s^- \rightarrow \\
(CH_3)_2N
\end{array}
\left[
\begin{array}{l}
(CH_3)_2N \\
(CH_3)_2N-\overset{\cdot}{P}-O-Y \\
(CH_3)_2N
\end{array}
\right]^*
\rightarrow
\begin{array}{l}
(CH_3)_2N \\
(CH_3)_2N-\overset{\cdot}{P}-O-Y + h\nu \\
(CH_3)_2N
\end{array}
$$

$$Y = I, p\text{-}CH_3C_6H_4SO_2, CH_3SO_2 \quad .$$

The iodine derivative was formed by the reaction between the solvent and elemental iodine liberated at the anode in potassium iodide solution, and the other two compounds were obtained

by adding tosyl chloride and mesyl chloride respectively to the solution.

The second group of processes accompanied by the emission of light consists of the reduction of neutral molecules with the simultaneous dissociation of the original molecule. In these processes the formation of the excited state often takes place at the stage of the addition of the second electron, after the dissociative one-electron reduction:[36]

$$(C_6H_5)_3CCl + e_s^- \rightarrow (C_6H_5)_3C^\cdot + Cl^- \qquad (C_6H_5)_3C^\cdot + e_s^- \rightarrow (C_6H_5)_3C^{\bar{*}} \quad .$$
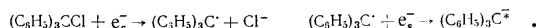
Reactions of this type include the reduction of N-toluene-sulphonylcarbazole, examined below, and the reduction of benzyl chloride and diphenylmethyl chloride.[35]

It is of interest to compare the direct cathodic reduction with the reduction of the same substance by solvated electrons. Thus the pseudo-phosphonium cations formed in solutions of iodine, tosyl chloride, and mesyl chloride in HMPA are reduced at potentials more than 2.5 V more positive than the potential of the generation of solvated electrons; this gives non-excited species.[37]

Similarly, N-tosylcarbazole is reduced at an electrode without luminescence at a potential which is 0.8 V more positive than the generation potential of solvated electrons:


(1)

(2)
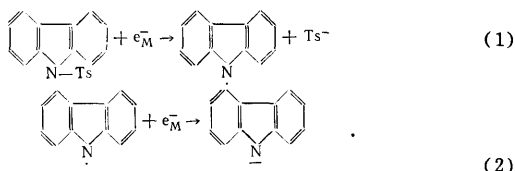
As always, chemiluminescence appears when the generation potential of the solvated electrons is reached. It is due to the reaction
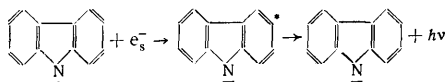
The process takes place similarly when HMPA is replaced by a mixture of ammonia and tetrahydrofuran in the volume ratio 2 : 1.[38]

This system is similar to that in pure ammonia. Tetrahydro-furan ensures the solution of the organic compounds. The reduction of α- and β-naphthol tosylates by solvated electrons in a mixture of ammonia and tetrahydrofuran leads to the emission of light:[38,39]

$$Naph{-}Ts + e_s^- \rightarrow Naph{-}Ts^{\bar{\cdot}} \rightarrow Naph^\cdot + Ts^-$$
$$Naph^\cdot + e_s^- \rightarrow Naph^{\bar{*}} \qquad .$$
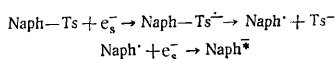
Chemiluminescence was also observed when solvated electrons were generated in a solution of sodium perchlorate in HMPA containing 9-chlorofluorene derivatives.[34]

Thus the study of chemiluminescence provides a useful method of studying the mechanism of the reduction of compounds by solvated electrons.

V. THE REDUCTION OF INDIVIDUAL CLASSES OF ORGANIC SUBSTANCES BY SOLVATED ELECTRONS

From the preparative viewpoint, the use of the electrochemical generation of solvated electrons is most effective for reducing substances which require high negative potentials for electron transfer or which are not reduced at all electrochemically. These compounds are aromatic hydrocarbons, alkenes, aliphatic ketones, amides. and nitriles.

1. Aromatic Compounds

The aromatic compound most difficult to reduce is benzene. It is polarographically inactive,[40] and does not undergo direct electrochemical reduction. Direct cathodic reduction of benzene does not take place in liquid ammonia in a background of potassium or methyltributylammonium iodide at silver or gold electrodes.[41]

Benzene does not react with solvated electrons obtained by dissolving alkali metals in liquid ammonia.[1] In the presence of proton donors, however, benzene ir hydrogenated under the influence of solvated electrons. Table 7 gives data obtained by different authors on the preparative electrochemical reduction of this compound, and shows that in some cases the process can be carried out fairly selectively and with a good current efficiency. Allowance must be made, however, for the fact that the data in Table 7 were generally obtained with incomplete transformation of the starting material. The high current efficiencies show that the proportion of side reactions is small. This agrees with the results of Schindewolf and Neumann,[49] which showed that solvated electrons obtained by laser photolysis in a mixture of ammonia and water (25 °C) containing benzene hydrogenate benzene and do not react with the components of the solvent (ammonia and water).

Table 7. Reduction of benzene in aprotic media.

No.	Solvent	Background	Proton donor	I, A cm^{-5} electrode	T, °C	Reduction product (%)	overall current efficiency, %	Refs.
1	Liquid ammonia	NaCl	ethanol 1–4%	2×10^{-2} platinum	−33	cyclohexa-1,4-diene (98)	41*	[42]
2	HMPA	LiCl	methanol	platinum	—	cyclohexa-1,4-diene (53) cyclohexa-1,3-diene (2) hexene (21) hexane (24)	—	[43]
3	Ditto	ditto	ethanol 67 mole %	9.0×10^{-2} aluminium	—	cyclohexadiene (23) cyclohexene (10) cyclohexane (67)	95 — —	[44]
4	Ditto	LiClO₄ 0.2 M	water 0.1 M	—	—	cyclohexa-1,3-diene	—	[18]
5	Methyl-amine	LiCl	solvent	10^{-1} platinum	−70	cyclohexene (100) cyclohexa-1,4-diene (95) cyclohexene (4)	49²* 49³* —	[45,46]
6	Ethylene-diamine	LiCl 0.3M	ditto	2×10^{-2} platinum	+25– 27	cyclohexadiene (17) cyclohexene (70) cyclohexane (13)	64 70	[47]²*
7	Ditto	LiCl, 0.3 M		7×10^{-2} carbon	33	cyclohexa-1,4-diene (38) cyclohexane (14.4)	52,4 —	[48]³*

Note. 1*) excess of benzene; 2*) diaphragm; 3*) without diaphragm, excess of benzene; 4*) diaphragm, excess of benzene.

The data in Table 7 illustrate the reduction of benzene in media typical of the electrochemical generation of solvated electrons. The addition of proton donors, however, may lead to appreciable reduction of benzene in mixtures of water

with aprotic solvents such as diglyme and sulpholane (Table 8). In these solvents also, the reduction apparently involves the formation of solvated electrons. Thus for example in a diglyme—water mixture the process takes place at a potential of -3.3 V (s.c.e.), which is sufficient for the generation of solvated electrons, and the potential is the same in the presence and in the absence of benzene.
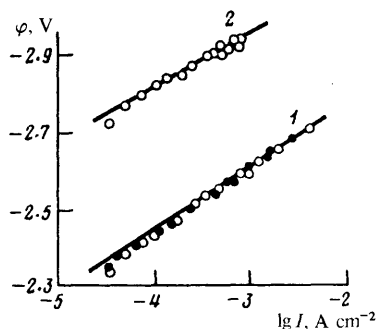

Figure 3. Dependence of the potential ϕ, V (s.c.e.) on the current density at a dropping mercury electrode in aqueous solutions ($c = 0.1$ M) at 20 °C; *1*) in solutions of tetramethyl-ammonium hydroxide and iodide; *2*) in a solution of tetra-butylammonium hydroxide.[58]

The increase in the proportion of products with a high degree of hydrogenation with increase in the concentration of proton donors is noteworthy (Table 9).

Table 9. Reduction of benzene in HMPA—ethanol mixture.[44]

Cathode	Donor, mole %	T, °C	I, A cm^{-2}	Reduction product, %		
				cyclohexadiene	cyclohexene	cyclohexane
Al	66.6	28	$9.1 \cdot 10^{-2}$	20.2	8.5	71.3
Al	5	28	$9.1 \cdot 10^{-2}$	81.2	16.4	2.3
Al	66.6	28	$3.6 \cdot 10^{-3}$	53.1	10.1	36.8
Al	66.6	-2	$3.6 \cdot 10^{-3}$	93.0	5.8	1.2
Pt	5	28	$9.1 \cdot 10^{-2}$	85.7	12.9	1.4

The favourable influence of a high concentration of proton donors on reductive hydrogenation is also observed in other cases. For example, aromatic sulphides and ethers are also reduced with the participation of solvated electrons generated at a cathode.[15] The cyclic voltammetric curves at a platinum electrode in solutions of lithium chloride in HMPA and its mixtures with ethanol (up to 50 mole %) in the presence of diphenyl sulphide coincided with the curves obtained without adding the organic substance. Table 10 gives the composition of the reduction products for different concentrations of alcohol in the solution, and shows that solvated electrons break the bond between sulphur and the carbon atom of the aromatic ring, with subsequent addition of a proton. In the absence of alcohol, the main reduction product is benzene,

Table 8. Reduction of benzene in protonic media.

No.	Solvent	Background	Electrode	T, °C	Reduction		overall current efficiency, %	Notes	Refs.
					product	%			
1	Water, diglyme	$(C_4H_9)_4NBr$ (12 g in 80 ml solution)	mercury*	25—30	cyclohexa-1,4-diene cyclohexene	96.3 3.7	71 —	diaphragm, excess of benzene	[50]
2	Water^{2*} 10 ml, ethyl-enediamine 40 ml	NH_4Cl, 2 g $(C_6H_{13})_4NBr$ 0.75^{4*}	graphite	—	cyclohexa-1,4-diene cyclohexane	50 2	52 —		
3	Water^{3*} 35.8^{4*} sulpholane^{5*} 52^{4*}	$(C_4H_9)_4NBr$ 3.7^{4*}	mercury	40	cyclohexa-1,4-diene	98.5	70.7	diaphragm, degree of trans-formation of benzene 32.8%, homogeneous catholyte	[52]
4	Diethyleneglycol 87.6^{4*}	$(C_4H_9)_4NBr$ 3.7^{4*}	mercury	—	cyclohexa-1,4-diene	91.1	68.1	diaphragm, degree of trans-formation of benzene 36%, homogeneous catholyte	[53]
5	Isobutyl^{4*} alcohol 87.6	$(C_4H_9)_4NBr$ 3.7^{4*}	mercury	40	cyclohexa-1,4-diene	91.2	48.9	diaphragm, degree of trans-formation of benzene 31.8%, homogeneous catholyte	[54]
6	Water	$[(C_4H_9)_4N]_2SO_4$ $(C_4H_9)_4NOH^{6*}$	mercury	65	cyclohexa-1,4-diene cyclohexene	87 13	77 —	cation-exchange membrane, excess of benzene, heterogeneous catholyte^{6*} with stirring	[55]
7	Water	$(C_4H_9)_4NOH^{7*}$, pH$>11^{8*}$	mercury	—	cyclohexa-1,4-diene		50^{9*}	without diaphragm, continuous supply of benzene and removal of product	[56,57]

* Electrolysis at a controlled potential of -3.3 V (s.c.e.); the potential is the same in the presence and in the absence of benzene.
^{2*} Or other amine containing 1—8 carbon atoms.
^{3*} Or a lower aliphatic (alicyclic) alcohol.
^{4*} Mole %.
^{5*} Or sulphoxide.
^{6*} $\{(C_4H_9)_4N\}_2SO_4 : (C_4H_9)_4NOH : H_2O : C_6H_6 = 20 : 1 : 71 : 8$ (by weight).
^{7*} Can be replaced by $(C_4H_9)_3C_2H_5NOH$ or $(C_3H_7)_4NOH$.
^{8*} At high pH values there is a decrease in the liberation of hydrogen and an increase in the stability of the steel anode.
^{9*} In a background of $(C_4H_9)_3CH_3NOH$ the yield decreases, and in a background of $(C_2H_5)_4NOH$ and $(CH_3)_4NOH$ reduction does not take place.

for the reduction of which the protons of impurities are sufficient. Without alcohol, benzene is stable to the action of solvated electrons, but in the presence of alcohol, benzene undergoes reductive hydrogenation, which is greater, the higher the concentration of alcohol in the solution.

Table 10. The reduction of diphenyl sulphide in solutions of lithium chloride (0.5 M) in mixtures of HMPA and ethanol, 15 °C.[15]

Alcohol, mole %	Yield of products, %						Trans-formation, %	Current efficiency, %
	benzene	cyclohexa-1,4-diene	cyclohexa-1,3-diene	cyclo-hexene	biphenyl	other sub-stances		
50	32.7	10.3	1.6	1.3	traces	0.8	46.4	67.2
35	42.1	8.2	1.1	1.3	traces	3.2	54.3	69.6
14	65.1	0	0	0	1.8	0	66.9	61.4
0	84.8	0	0	0	1.8	2.4	88.9	79.4

An interesting feature is that benzene can be reduced not only in a mixture of an aprotic and a protonic solvent but also in purely protonic media. Thus dihydric and monohydric alcohols, and also water, have proved suitable for this purpose (Table 8).

In aqueous tetrabutylammonium hydroxide solution, the potential of a mercury cathode is displaced to between - 2.5 V and -2.8 V (Fig.3),[58] which is sufficient for the generation of solvated electrons (see Table 1). Tetrabutylammonium cations are adsorbed on the electrode surface, displacing water molecules and hindering their discharge at the electrode.

When purely aqueous solutions are used, a complication not encountered in organic systems arises, due to the low solubility of benzene and many other organic compounds in water (20 °C, M):[59-61]

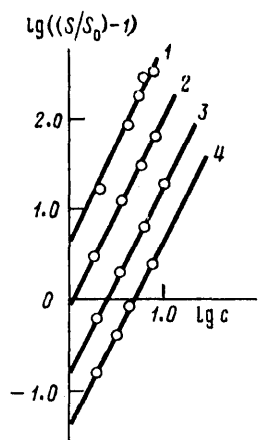|	
Benzene	$2 \cdot 10^{-2}$; $2.4 \cdot 10^{-2}$ (25°C)
Toluene	$6 \cdot 10^{-3}$
o-, m-, and p-Xylenes	$1.6 - 1.8 \cdot 10^{-3}$
Phenol	$9 \cdot 10^{-1}$
α-Naphthol	$3 \cdot 10^{-4}$

Figure 4. Solubility of benzene at 25 °C in solutions of the bromides: 1) tetrabutylammonium; 2) tetrapropylammonium; 3) tetraethylammonium; 4) tetramethylammonium; S is the solubility in the solution; S_0 is the solubility in water.[60]

The solubility decreases in the order benzene–toluene–ethylbenzene–mesitylene (1.6–0.6–0.2–0.05 g litre^{-1}).[60]

It should be noted, however, that in the presence of tetraalkylammonium cations the solubility of organic compounds increases[61-64] (the "salting-in" effect). The solubility is higher, the higher the concentration of the salt and the longer its alkyl group (Fig.4),[60,61] and also on going from chlorides to bromides and iodides.[64]

The reduction of benzene can also be carried out in a heterogeneous system (emulsion) with vigorous stirring (Table 8). The movement of benzene to the electrode is apparently facilitated by the presence on the elrctrode surface of the electrical double layer of tetrabutylammonium cations, which should help to bring benzene on to the electrode surface.

An examination of different mechanisms of mass transfer and charge transfer in the electrolysis of an emulsion (organic substance–water) showed that an important positive role is played by the hydrophobic tetra-alkylammonium cations.[59]

The behaviour of toluene is analogous to that of benzene. Toluene is also polarographically inert, and does not react with solvated electrons obtained by dissolving alkali metals in liquid ammonia,[1] but it can be reduced by solvated electrons in aprotic, mixed, and protonic media (see Table 11).

Table 11. The reduction of toluene.

Solvent	Background	Proton donor	Elec-trode	Product (%)	Refs.
HMPA	LiClO₄ NaClO₄	H₂O ≤ 0.1 M	Pt	1-methylcyclohexa-1,4-diene	[18]
HMPA	LiCl	C₂H₅OH 67 mole %	Al	methylcyclohexane (45.4)	[25]
Methylamine	LiCl	solvent	Pt	methylcyclohexadiene (94)¹*	[45¹*,
Ditto	LiCl	ditto	Pt	methylcyclohexene (5)¹* methylcyclohexane (86)²* toluene (14)²*	46²*]
Diglyme–water	(C₄H₉)₄NBr	H₂O	Hg³*	1-methylcyclohexa-1,4-diene (95)	[50]⁴*
Diethylene glycol	(C₄H₉)₄NBr	solvent	Hg	1-methylcyclohexa-1,4-diene	[53]
Isobutyl alcohol	(C₄H₉)₄NBr	ditto	Hg	1-methylcyclohexa-1,4-diene	[54]
Water	(C₄H₉)₄NOH	»	Hg	reduction	[56]

Note. 1*) without diaphragm, current efficiency 64%; 2*) with diaphragm, current efficiency 44%; 3*) electrolysis at a potential of -3.3 V (s.c.e.), which is the same in the presence and in the absence of toluene; 4*) current efficiency 61%.

As in the case of benzene, it is possible to select conditions under which the process is fairly selective. The maximum degree of reduction is obtained in a mixed solvent at a high concentration of the protonic component (Table 11).

Table 12 compares the results of the reduction of other aromatic compounds: naphthalene, tetralin (tetrahydronaphthalene), anthracene, and dihydroanthracene, in media in which the cathodic generation of electrons is possible. Like benzene and toluene, tetralin is not reduced at an electrode, for example at mercury in ethylenediamine,[48] but is effectively hydrogenated with the participation of solvated electrons (Tables 12 and 13).

Unlike benzene, toluene, and tetralin, naphthalene and anthracene can be reduced directly at an electrode. Thus in anhydrous ethylenediamine, naphthalene is active at mercury and platinum electrodes.[47,48] The product of the reduction of naphthalene in protonic media is 1,4-dihydronaphthalene.[67] For example, the preparative direct electrode

reduction of naphthalene in a mixtpre of acetonitrile and water gives 98% 1,4-dihydronaphthalene mixed with small quantities of 1,2-dihydronaphthalene and tetralin with an overall current efficiency of 86%.[68]

Table 12.   The reduction of naphthalene, anthracene, and their derivatives by electrolysis in HMPA and ethylenediamine.

Medium	Proton donor	Electrode	I, A cm^{-2}	Substance	Reduction products (%)	Current efficiency, %	$E_{1/2}^{*}$	Refs.
LiCl (HMPA)	C$_2$H$_5$OH 67 mole % (33 vol.%)	aluminium	9.1·10^{-2} (—2.4± 0.1)^{2*}	naphthalene	dihydrona-phthalene (7) tetralin (22) hexalin (20) octalin (11) decalin (40)	96	—2.5	[44]^{3*}
LiCl (HMPA)	C$_2$H$_5$OH^{4*} 67 mole % (33 vol.%)	aluminium	—2.4 V^{2*}	tetralin	hexalin (10) octalin (5) decalin (85)	54	—	[65]$^{5*,\,6*}$
LiCl, (C$_4$H$_9$)$_4$N (ethylene-diamine)	solvent	platinum graphite carbon		tetralin^{7*}	hexalin octalin	—	—	[48]^{8*}
LiCl (HMPA)	CH$_3$COOH 1 M	lead	2·10^{-3*}	anthracene	dihydro-anthracene (100)	65	—2.0	[66]
LiCl (HMPA)	CH$_3$COOH 1 M	glass-carbon	5·10^{-3}		di- (2), tetra- (3), hexa- (88), and octa-anthracene10*	57	—	
			1.3·10^{-1}		tetra- (15) and hexa-anthracene (85)	53	—	
LiCl (HMPA)	CH$_3$COOH 1M	aluminium	1.5·10^{-1}	dihydro-anthracene	tetra- (70) and hexa-anthracene (30)	—	—	[66]

Note: *) half-wave potentials (s.c.e.) for the reduction of the substances in a mixture of 75% dioxan + 25% water in a background of tetraethylammonium or tetrabutylammonium iodide;[40] 2*) potential relative to a silver wire in the same solution, which is the same for benzene, naphthalene, and tetralin; 3*) with a diaphragm; 4*) there is practically no reduction in the absence of a proton donor; 5*) polaro-graphically inactive; 6*) with diaphragm; 7*) see Table 13; 8*) without diaphragm; 9*) generation of electrons does not take place at this current density; 10*) traces of the last compound.

Table 13.   Reduction of tetralin by electrolysis in ethylene-diamine.[48]

Background	T, °C	Electrode*	Current efficiency, %^{2*}	Products^{3*} hexalin	Products^{3*} octalin
Lithium chloride	33.0	platinum graphite carbon	57.9 70.5 80.3	41.6 55.4 67.3	7.5 11.6 9.5
Tetrabutylammonium iodide	28.0	ditto	17.0	13.0	1.8
Ammonium chloride	20.0	ditto	0	0	0

Note: *) current density 7 × 10^{-2} A cm^{-2}; 2*) a small fraction of the current is used for the reduction of dihydronaphthalene (impurity in tetralin); 3*) fraction of the current.

In a solution of lithium chloride in HMPA, anthracene gives two cathodic peaks: a peak due to the reversible formation of a radical-anion (+1.23 V)† and a peak due to the irreversible formation of the dianion (+0.33 V)#.[66] As a proton donor is added, a second peak gradually appears beside the first, that is as in the case of naphthalene, hydrogenation of one bond takes place.   Tables 12 and 13 show that more extensive hydrogenation takes place under the influence of solvated electrons.   Analysis of the preparative electrolysis data shows that, irrespective of the electrode material, the reduction gives a mixture of dihydro-, tetrahydro-, and hexahydro-anthracenes.   The change in the concentration of these products as electrolysis proceeds (see Fig.5) shows that the reduction takes place in stages, and a more detailed study of the kinetics of the process indicates that the formation of tetrahydroanthracene takes place partly without the stage of dihydroanthracene formation:
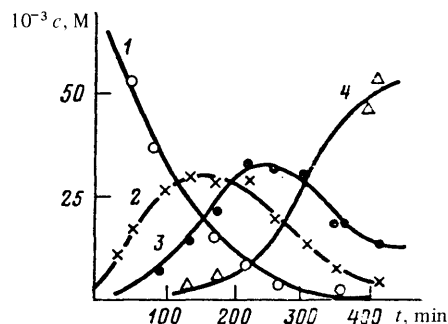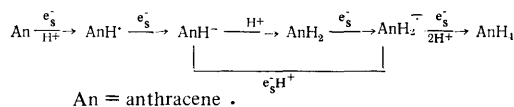
$$An \xrightarrow[H^+]{e_s^-} AnH^{\cdot} \xrightarrow{e_s^-} AnH^- \xrightarrow{H^+} AnH_2 \xrightarrow{e_s^-} AnH_2^- \xrightarrow[2H^+]{e_s^-} AnH_4$$

$$\underset{e_s^-H^+}{\underbrace{\qquad\qquad\qquad}}$$

An = anthracene .

Figure 5.   Change in the concentration of anthracene (c) and its reduction products at a current density of 1.25 × 10^{-1} A cm^{-2}; initial anthracene concentration 0.070 M; 1) anthracene; 2) dihydroanthracene; 3) tetrahydroanthracene; 4) hexa-hydroanthracene.[66]

Interesting data were obtained[69] on the reduction of naph-thalene on platinum in mixtures of alcohols (methanol, ethanol, propan-1-ol, and propan-2-ol) with HMPA in a background of lithium chloride at a high concentration of the protonic com-ponent.   Naphthalene is not reduced in pure ethanol§.   When 10—50 vol.% HMPA is added at a potential which is 1 V more negative than the potential of the electrode reduction of naph-thalene, the latter is converted into a mixture of dihydro-naphthalene, tetralin, hexalin, and decalin.   The value of

†The potentials are given relative to a lithium reference electrode; on this scale, the potential at which the generation of electrons starts is +0.16 V.

#The direct reduction of anthracene can also be carried out in ethylenediamine.[47]

§ Tetralin also could not be reduced in ethanol containing lithium chloride.[65]

the potential and the nature of the products indicate that the reaction involves solvated electrons, in spite of the high concentration (up to 90 vol.%) of alcohol in the solution.

The example of aromatic compounds illustrates a characteristic feature of reduction by solvated electrons: the rate of the process is independent of the nature of the organic substance. Thus in HMPA, the reduction potentials of benzene, naphthalene, and tetralin coincide.[55] There are very few published data on the reduction of an aromatic ring in compounds containing functional groups. In the HMPA—ethanol system at an aluminium cathode, phenol and anisole are reduced to cyclohexanol and methoxycyclohexane respectively in yields of 51.7% and 45.8%.[25]

2-Naphthyl ethers are reduced selectively to dihydro-compounds, whose hydrolysis gives tetralones which are the starting materials for the synthesis of medicinal products.

$$\text{(naphthalene)}-OCH_3 \xrightarrow{2e_s^-.2H^+} \text{(dihydronaphthalene)}-OCH_3 \rightarrow \text{(ketone)}=O .$$
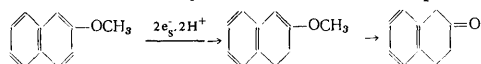
This process has been carried out on a large scale.[70]

2. Unsaturated Compounds

Table 14 gives data on the reduction of alkenes in systems in which the cathodic generation of electrons is possible. It cannot be concluded, however, that the reaction involves the formation of solvated electrons in all cases. In solutions of lithium chloride and tetrabutylammonium tetrafluoroborate in HMPA, 1,1-diphenylethylene and tetraphenylethylene are reduced directly at a mercury electrode.[74]

Table 14. The reduction of alkenes by electrolysis in HMPA and methylamine.

Medium	Proton donor	Alkene	Reduction product	Refs.
LiBr, HMPA	without donor	$(C_6H_5)_2C{=}CH_2$	$[(C_6H_5)_2C(CH_2)_2C(C_6H_5)]_2^{-*}$	[71]
NaI, HMPA	without donor	$(C_6H_5)_2C{=}C(C_6H_5)_2$	$[(C_6H_5)_2C{-}C(C_6H_5)_2]^{2-}$	[71]
LiCl, HMPA	C_2H_5OH 67 mole %	$(CH_3)_2C{=}C(CH_3)_2^*$	$(CH_3)_2CHCH(CH_3)_2$	[44]
LiCl, methyl-amine	without donor	1-octene	octane 51%[3*]	[72]
LiCl, HMPA	C_2H_5OH 5-50 vol.% C_3H_7OH 10-50 vol.%	cyclo-octa-1,5-diene	cyclo-octane cyclo-octene[4*]	[73]

Note: *) hydrolysis gave a high yield of tetraphenylbutane; 2*) the alkene $(CH_3)_2C = C(CH_3)_2$, which shows steric hindrance, is reduced in 30% yield at practically the same rate as hex-1-ene and hex-2-ene; 3*) the rest is the starting material (2% in unchanged form, 47% in the isomerised form); 4*) the proportion of cyclo-octene increases on going from ethanol to propanol and with decrease in the concentration of alcohol and increase in the current density.

It is of interest to compare the reactivities of alkene and aromatic bonds towards solvated electrons. Table 14 shows that in a number of cases only alkene bonds are reduced. This is characteristic of short alkene bonds¶. Thus the main

¶ This agrees with data[75] which show that α-alkenes from pentene to decene are more difficult to reduce by metallic sodium in liquid ammonia than a longer alkene.

product of the reduction of styrene in a solution of lithium chloride in methylamine (proton donor—solvent) is ethylbenzene (~70%),[72] and allylbenzene gives n-propylbenzene. If a stronger proton donor (ethanol) is added, the aromatic ring begins to be hydrogenated instead of the alkene bond, and the main product of the reduction of allylbenzene is 2,5-dihydroallylbenzene. The highest selectivity in methylamine in the presence of ethanol was achieved[72] for 5-phenylpent-2-ene, which gave 83% 2,5-dihydro-5-phenylpent-2-ene.

3. Ketones

Other compounds difficult to reduce are aliphatic ketones, which are reduced at potentials more negative than −2.0 V (s.c.e.).

A number of ketones illustrate another characteristic feature of the reduction of organic compounds by solvated electrons, namely the high stereospecificity of the process. In particular, the products of the reduction of alkylcyclohexanones and alkylcyclopentanones are alcohols in two stereoisomeric forms. Preparative data for these compounds are given in Table 15. The proton donor in all cases was ethanol.

Table 15. Reduction of alkylcyclopentanones and alkylcyclohexanones by solvated electrons generated in HMPA.

No.	Ketone, mass % in the catholyte	Ketone : Donor	Electrode	Current efficiency, %	trans-Isomer, %	Method of reduction*	Refs.
1	2-Methylcyclopentanone, 2	1:2	copper	83.5	90.2	2	
2	2-Methylcyclopentanone, 2	1:2	copper	88	90.6	1	
3	2-Methylcyclopentanone, 0.5	1:4,5	platinum	56.2	86.4	2	[76]
4	2-Methylcyclopentanone, 1	1:4,5	copper	78.5	93.7	2	
5	2-Ethylcyclopentanone, 2	1:2	copper	71.7	93.4	2	
6	2-Ethylcyclopentanone, 2	1:2	copper	84.8	89.3	1	
7	2-Methylcyclopentanone	1:1	copper	polymer		2	
8	4-t-Butylcyclo-hexanone	4 mole % alcohol	platinum	87	95	1	[77]
9	3,3,5-Trimethylcyclo-hexanone	10 mole % alcohol	5.9×10^{-2} A cm^{-2}	50	91	1	

*1) The total quantity of substance to be reduced (and the proton donor) was added to the catholyte, and electrolysis was carried out until the stable colour of solvated electrons appeared; 2) the starting material (and the proton donor) was added to the catholyte containing previously generated electrons; the quantity of starting material added left a slight excess of solvated electrons; the whole procedure was repeated many times; Nos.1—7—sodium bromide; Nos.8 and 9—lithium chloride.

Table 15 shows that the cathode material and the method of reduction have no influence on the isomeric composition of the alcohol (the *trans*-form predominates†), whereas the electrode reduction gives a mixture of *trans*- and *cis*-carbinols, the ratio of which depends on the electrolysis conditions.[76] This indicated that in all cases the ketones are reduced by solvated electrons generated at the cathode, and this is confirmed by

† High stereospecificity was also observed in the reduction of stilbenes in monoglyme by solvated electrons obtained by dissolving potassium; *trans*- and *cis*-stilbenes $C_6H_5CH = CHC_6H_5$ give the same radical-anion with the *trans*-configuration.[78]

the polarisation curves(Fig.6). Curve *1*, recorded in the presence of methylcyclopentanone and ethanol, lies in the range of generation potentials of solvated electrons (curve *2*). The slight displacement of the curve towards negative potential values in the presence of the ketone is due to the passivation of the surface as a result of the polymerisation of reduction products. Fig.6 gives for comparison curve *3*, corresponding to the case where the generation of electrons is accompanied by a second cathodic process, namely the cathodic liberation of hydrogen. Thus the reduction of cyclic ketones takes place according to the scheme

$$H_2C-\overset{\underset{\displaystyle |}{H}}{\underset{\displaystyle |}{C}}-CH_3 \;\; H_2C\;\;\;\; C=O \;\;\; +2e_s^- \;+2H^+ \rightarrow \;\; H_3C-\overset{\underset{\displaystyle |}{H}}{\underset{\displaystyle |}{C}}-CH_3 \;\; H_2C\;\;\;\; C\overset{OH}{\underset{H}{\diagdown}} \;.$$
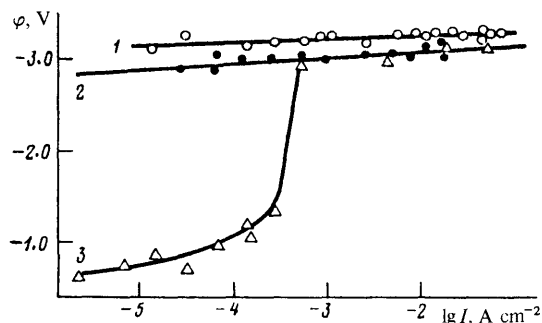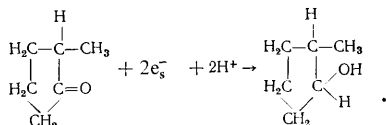
Figure 6. Dependence of the potential ϕ, V (s.c.e.) on the current density at a stationary copper electrode in HMPA at 25 °C: *1*) lithium chloride 0.2 M + methylcyclopentanone 1.8 × 10^{-2} M + ethanol 3.1 × 10^{-2} M; *2*) lithium chloride 0.2 M; *3*) lithium chloride 0.1 M + sulphuric acid 2.2 × 10^{-2} M.[76]

Similarly, solvated electrons generated at a cathode in a solution of lithium chloride in methylamine have been used[79] to reduce a number of ketones to the corresponding alcohols, namely heptan-2-one, pentan-3-one, cyclohexanone, and cyclopentanone. Electrons obtained by dissolving lithium, sodium, and potassium in HMPA have been used to reduce the ketone $C_6H_{13}COCH_3$, with t-butyl alcohol as proton donor.[80]

Alkali metals in liquid ammonia have been used[81] to reduce various substituted bicyclohexanones (bicyclo[3,1,0]hexa-3-en-2-ones).

The behaviour of acetylcyclopropanes deserves special examination. The reduction by an active metal in liquid ammonia takes place with opening of the ring:[82,83]
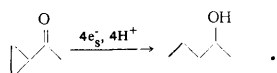
If the same reaction is carried out with electrochemically generated solvated electrons at a mercury or platinum cathode in liquid ammonia using tetraethylammonium tetrafluoroborate as background electrolyte, the chief electrolysis product is 3-methylhexan-3-ol. It is suggested that in this process the tetraethylammonium cations can act as an alkylating agent.
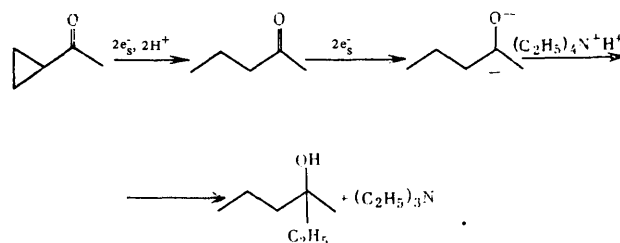
4. Carboxylic Acid Derivatives—Amides, Nitriles, and Esters

Electrochemically generated solvated electrons have been used to reduce various other organic compounds.
The data for aliphatic amides are given in Table 16.

Table 16. The reduction of aliphatic amides by solvated electrons generated at a cathode.

Medium	Proton donor	Amide	Reduction product, %	Refs.
LiCl + HMPA	acetic, oxalic, hydrochloric acids	CH_3CONH_2	ethanol, ethylamine*	[84]
LiCl + methylamine	solvent	$CH_3(CH_2)_4CONH_2$	alcohol, 58	
		$CH_3(CH_2)_8CONH_2$	ditto, 59	
		$CH_3(CH_2)_{12}CONH_2$	» 92	
		$CH_3(CH_2)_{14}CONH_2$	» 86	
		$CH_3(CH_2)_{16}CONH_2$	» 79	
		$CH_3(CH_2)_4CONHCH_3$	» 51	[79, 85]
		$CH_3(CH_2)_8CONHCH_3$	» 81	
		$CH_3(CH_2)_8CON(CH_3)_2$	» 93	

*Decrease in temperature and the current density, and increase in the acidity, increase the proportion of amine.

Table 16 shows that solvated electrons can reduce aliphatic amides to alchols in good yield. In a medium of methylamine, the alcohol is formed if the solvent itself acts as proton donor. When ethanol, which is a stronger proton donor, is added to methylamine, the yield of alcohol decreases sharply, and the aldehyde becomes the main reaction product.[79,85]
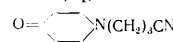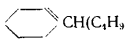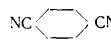
In the reduction of acetamide in HMPA, the reduction products are ethylamine and ethanol. When the process is carried out at room temperature, the main reduction product is ethanol, but at a lower temperature (~11 °C), the two products are formed in approximately equal quantities. A low current density and more acidic proton donors (for example hydrogen chloride) also favour the formation of the amine. To explain the observed regularities, it was suggested that the first stage of the reduction is the formation of an unstable aminoalcohol, which undergoes decomposition depending on the acidity of the medium:
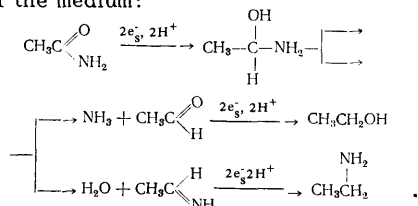
Ethanol is formed in basic catalysis, whereas another route, giving the amine, is followed preferentially in an acidic medium.

Published data on the reduction of nitriles and dinitriles are summarised in Table 17#.

Table 17. Reduction of nitriles and dinitriles by solvated electrons.[86-89]

| Method of generating electrons	Nitrile	Product (%)	
Cathodic generation in a solution of lithium perchlorate in HMPA*	CH₃CN CN(CH₂)₄CN	C₂H₅NH₂ H₂N(CH₂)₄NH₂ H₂N(CH₂)₅CN	
Ditto	CH₂=CH₂CN CN—CH₂CN	CH₃(CH₃)₂NH₂ H₂N(CH₃)₂CN H₂N(CH₂)₃NH₂	
Solution of potassium in hexa-methylphosphortriamide²*	C₇H₁₅CN C₁₀H₂₁CN C₁₇H₃₅CN	C₇H₁₆ C₁₀H₂₂ C₁₇H₃₆	(80) (90) (80)
	H₁₃C₆ | CHCN | CH₂=CHCH₂	dec-1-ene C₁₀H₂₂	(32) (32)
	(CH₃)₂C—CN | C₇H₁₅	2-methylnonane	(89)
	O=⟨ ⟩N(CH₂)₃CN	O=⟨ ⟩NC₃H₇	(76)
	CH₃ \>CH(CH₂)₂C(CH₂)₂CN CH₃	2,5-dimethylhexane	(76)
	Ph\ \>CHCN C₄H₉	allylbenzene ⟨ ⟩C₃H₁₁	(34) (26)
	C₄H₉ Ph—C—CN C₄H₉	Ph—CH(C₄H₉)₂ ⟨ ⟩CH(C₄H₉)₂	(56) (16)
	CH₃ Ph—CH₂—C—CN CH₃	PhCH₂CH(CH₃)₂ (with and without alcohol)	(80—85)
Solution of sodium in liquid ammonia³*	Ph₃CCN Ph₂CHCN PhCH₂CN PhCN [(CH₃)₂NC₆H₄]₃CCN	Ph₃CH Ph₂CH₂ PhCH₃ C₆H₆ [(CH₃)₂NC₆H₄]₃CH	(90) (76) (90) (93)
Solution of lithium in liquid ammonia	NC⟨ ⟩CN	⟨ ⟩	(43)
		CH₃CHCH₂CH₂CH₃ | CH₃	(37)
		CH₃CH₂CHCH₂CH₃ | CH₃	(18)
Solution of lithium in ethylamine	n-C₁₂H₂₅CN	n-C₁₂H₂₆ n-C₁₃H₂₇NH₂	(35) (65)
Cathodic generation in a solution of lithium chloride in ethylamine	dehydroabietonitrile cycloheptyl cyanide n-octyl nitrile	dehydroabietane cycloheptane n-octane	

Note. *) Sufficient nitrile and ethanol (proton donor) was added by means of a micro-burette to a solution in which solvated electrons had previously been generated, to leave a slight excess of electrons; the procedure was repeated many time; 2*) the co-solvent t-butyl alcohol was used as proton donor, although in the authors' opinion the role of donor may be played by HMPA; 3*) the alkali metal was dissolved in ammonia, the nitrile was added, the ammonia was removed, and hydrolysis was carried out.

The reduction of nitriles to amines also takes place by direct electrode reduction in solutions of hydrochloric and sulphuric acids in ethanol at palladium or nickel black cathodes (benzo-nitrile to benzylamine, and benzyl cyanide to β-phenylethyl-amine).[90]

Solvated electrons, generated at a cathode or obtained by dissolving an alkali metal, have been used to reduce nitriles. Table 17 shows that in general, two reactions may take place: decyanation to give the hydrocarbon

$$RCN + 2e_s^- + 2H^+ \to RH + HCN$$
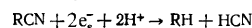
and reduction to the amine

$$RCN + 4e_s^- + 4H^+ \to RCH_2NH_2 \ .$$
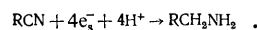
The amine group formed is inert towards solvated electrons. Judging from available data on reduction by solvated electrons, the more characteristic reaction is the removal of the nitrile group (decyanation), which probably takes place via a radical-anion stage. Thus the following scheme has been proposed[91] for the reduction of dehydroabietonitrile by sodium in liquid ammonia:
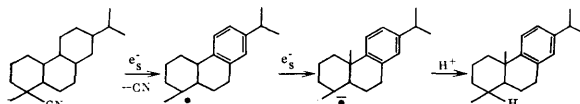
Nitrile groups on neighbouring carbon atoms are removed with the preferential formation of carbon—carbon multiple bonds, for example:
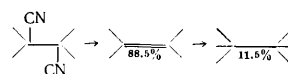

Interesting transformations are undergone by 1,4-dicyano-cyclohexane under the influence of solvated electrons:[88]
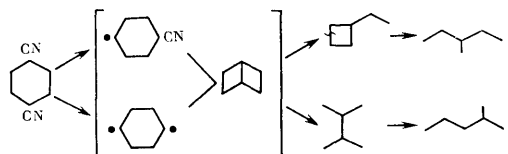
The final reaction products are 3-methylpentane and 2-methyl-pentane.

The nitrile group is apparently more reactive towards solvated electrons than the alkene bond or the bonds of the benzene ring, but the latter may be partly hydrogenated after the nitrile group has been reduced (Table 17).

Solvated electrons also reduce esters.[92] In particular, dimethyl adipate gives hexane:

$$CH_3O\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow[-2H_2O]{12H^+, 12e_s^-} C_6H_{14} + 2CH_3OH$$
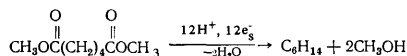
that is the reduction takes place with rupture of the C—O bond. There are no published quantitative data on this reaction.

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The material of the present review shows that electro-chemically generated solvated electrons can be used success-fully to reduce various organic compounds, many of which are electrochemically inactive, that is at the potentials attainable in polar solvents (between -2.5 V and -2.8 V, s.c.e.) there is practically no electron exchange between an electrode and the molecules of these organic substances. Thus the electro-chemical generation of solvated electrons extends the pos-sibilities in preparative electrochemical synthesis.

Another advantage of this method is that the actual generation of the solvated electrons can be carried out with high current densities, irrespective of the concentration of organic substance in the solution. This feature is important when it is necessary to carry out the exhaustive reduction of a substance present in solution at a low concentration. Thus the use of solvated electrons can be regarded as one possible way of intensifying electrochemical processes.

The first work on the generation of solvated electrons was carried out in liquid ammonia, and slightly later, HMPA began to be used as solvent. Both of these solvents are inconvenient to use. Ammonia can be used only at low temperatures of about −30 °C, and HMPA has a high boiling point, so that the separation of pure reduction products from it is difficult. In this connection it is worth noting recently published data on the possibility of generating electrons in solutions containing a large quantity of protogenic solvents, or even in aqueous solutions, containing 25—40% tetrabutylammonium salts. The change to these media simplifies considerably the procedure for generating solvated electrons, making it comparable with the ordinary electrochemical process. This version of electro-reduction by solvated electrons should apparently find preparative application in laboratory practice and in various industrial processes.

The reduction of organic substances with the participation of solvated electrons can be regarded as a particular case of reactions involving electron carriers, which may be either organic or inorganic compounds. The use of solvated electrons, however, has at least two advantages: it is not necessary to introduce additional reagents into the reaction mass, and in preparative electrolysis this facilitates the separation of the reaction products; and there are processes such as, for example, the reduction of amides or certain aromatic compounds, which can be carried out only using solvated electrons. From these viewpoints alone, the use of solvated electrons in the electrosynthesis of organic substances appears promising and worthy of further study.

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