Supporting Electrolyte in Indirect Electrolytic Reactions

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With LiCl as supporting electrolyte electron transfer in solution may take place between a stable anion radical $A^{\cdot-}$ and a compound BX, forming an unstable anion radical, even if the polarographic wave of BX is masked by the reduction of Li^+. With tetrabutylammonium iodide (TBAI) as supporting electrolyte, electron transfer from an anion radical to the cation may occur with formation of tetrabutylammonium radical which decomposes slowly into tributyl-amine and butyl radical; the butyl radical may couple with the anion radical. Indirect reduction of a difficultly reducible compound BX may, however, take place, if the radical anion $BX^{\cdot-}$ decomposes much faster than the tetraalkyl-ammonium radical.

In connection with the present series on indirect electrolytic reactions of organic compounds [1] some aspects of the rôle of supporting electrolyte in such reactions have been investigated. At a mercury electrode, amalgam formation often is the cathodic potential-limiting reaction, and the idea of the work described below is to investigate the possible circumvention of this potential-limiting reaction by use of stable anion radicals $A^{\cdot-}$ as reagents for transferring electrons to compounds (BX), which form unstable anion radicals.
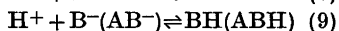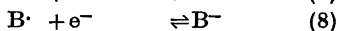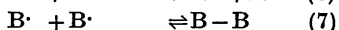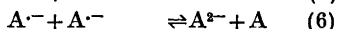
Lithium chloride and tetrabutylammonium iodide (TBAI) have been chosen as examples of supporting electrolytes; the solvent was in all cases (nominally) anhydrous N,N-dimethyl-formamide (DMF).

RESULTS AND DISCUSSION

Lithium chloride. The half-wave potential of 2-chloropyridine (I) is in DMF containing 0.1 m TBAI -2.27 V *vs.* aqueous saturated calomel electrode (aq. S.C.E.), which is more negative than the foot (~ -2.1 V (aq. S.C.E.)) of the reduction wave of 0.1 m LiCl in DMF. A polarogr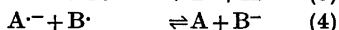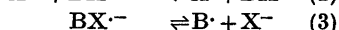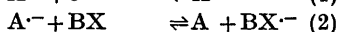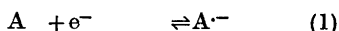aphic wave of 2-chloropyridine is thus not visible, when the dropping mercury electrode (DME) is used in DMF containing LiCl.

The polarographic half-wave potential of anthracene (II) in DMF/TBAI is -1.91 V *vs.* aq. S.C.E.; an anion radical which is stable in the absence of protons is formed in the electrode reaction; anthracene may thus be used as an A-compound [1] in the scheme below. 2-Chloropyridine on electron transfer forms an unstable anion radical which rapidly decomposes into chloride ion and pyridine radical, thus acting as a BX-compound [1] in the scheme below.

$$
\begin{aligned}
A \ +e^- &\rightleftharpoons A^{\cdot-} &(1)\\
A^{\cdot-}+BX &\rightleftharpoons A \ +BX^{\cdot-} &(2)\\
BX^{\cdot-} &\rightleftharpoons B^{\cdot}+X^- &(3)\\
A^{\cdot-}+B^{\cdot} &\rightleftharpoons A \ +B^- &(4)\\
A^{\cdot-}+B^{\cdot} &\rightleftharpoons AB^- &(5)\\
A^{\cdot-}+A^{\cdot-} &\rightleftharpoons A^{2-}+A &(6)\\
B^{\cdot} \ +B^{\cdot} &\rightleftharpoons B-B &(7)\\
B^{\cdot} \ +e^- &\rightleftharpoons B^- &(8)\\
H^++B^-(AB^-) &\rightleftharpoons BH(ABH) &(9)
\end{aligned}
$$
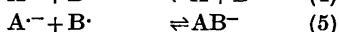
2-Chloropyridine is reduced at a potential of about 0.4 V more negative than that of anthracene, so the equilibrium (2) is shifted far to the left; the rapid decomposition of the 2-chloropyridine anion radical (3) forces, however, the reaction (2) to proceed from left to right.

In the polarography of anthracene (II) in DMF/0.1 m TBAI in the presence of 2-chloro-pyridine (I) an indirect reduction of I is indicated by an increase of the limiting current of II, a so-called catalytic wave. A rate constant of the catalyzing reaction of 75 m^{-1} s^{-1} was

found by a calculation according to Koutecký.[2] A similar catalytic wave is found in DMF containing LiCl and the rate constant is, within the experimental uncertainty, the same; if the small difference found is significant, the rate constant in DMF/LiCl is slightly higher than in DMF/TBAI.

A preparative reduction of 2-chloropyridine by means of electrolytically generated (and regenerated) anthracene radical anions produced pyridine in high yield (83 – 86 %), regardless of whether LiCl of TBAI was the supporting electrolyte. (4) rather than (5) is followed by 2-chloropyridine as with all aromatic BX-compounds investigated so far.

These results show that with a lithium salt as supporting electrolyte electron transfer is possible from an A-compound to a BX-compound, even if the polarographic wave of the BX-compound is masked by the reduction wave of lithium ions.

The electrode reaction of lithium ions at a mercury electrode is the formation of lithium amalgam which takes place at a potential much less negative than the reduction potential of Li^+ at an inert eletrode. In solution the tendency of electron transfer from an anion radical $A^{\cdot-}$ to a lithium ion (possibly participating in some kind of ion-pairing) is determined by the difference in redox potentials (at an inert electrode) of $A/A^{\cdot-}$ and Li^+/Li; this tendency is extremely small when the potential difference is one volt or more, which is the case when A gives a polarographic wave with LiCl as supporting electrolyte. The use of an electron transfer reagent, such as an anion radical, thus makes it possible by the indirect method to reduce at a mercury electrode certain substrates with a cheap, amalgam-forming cation, such as Li^+ or Na^+, as supporting electrolyte, even if a direct electrolytic reduction at a mercury electrode in that medium does not seem possible judging from polarographic data.

The present paper is not concerned with whether the electron transfer from the anion radical to the BX compounds is following (2) or the electron donating species is A^{2-}, formed in (6), or via some other route; this will be discussed in a later communication.

Tetrabutylammonium iodide (TBAI). Tetrabutylammonium iodide is usually an "inert" supporting electrolyte, but in the presence of a strong base it may act as a proton donor; the loss of a proton results in a Hofmann elimination with formation of butylene and tributylamine.

In the present context it is also of interest to know whether the tetrabutylammonium ion may accept an electron from an anion radical;[3] the resulting neutral radical would be expected either to lose the electron again or to decompose into tributylamine and a butyl radical, the salt thus acting as a BX-compound in the scheme.

It has been found [4] that in an indirect reduction, where the BX-compound is aliphatic, the aromatic anion radical $A^{\cdot-}$ and the aliphatic radical $B^{\cdot}$, formed in (3), may couple to AB^- (5), which then accepts a proton to ABH.

An anion radical could then conceivably react with TBAI in two ways, it could abstract a proton from it or it could transfer an electron to it. The outcome of this competition would depend on factors such as basicity of the anion radical, decomposition rate of the quaternary ammonium radical, and redox potential of the compounds in question. Again, a similar situation is found if the aromatic dianion (6) is the electron-transferring species.

The limiting current of an A-compound and the coulometric data might thus depend on the concentration and the nature of the supporting electrolyte; with 2-methylnaphthalene ($E_{\frac{1}{2}} = -2.42$ V vs. S.C.E. in DMF/TBAI) only a very small increase, if any, of the limiting current is observed on increasing the concentration of TBAI and this might just as well be due to an increase in the concentration of the proton donor, TBAI; a catalytic reaction could thus not be proved from polarographic data.

A preparative reduction of 2-methylnaphthalene in DMF containing 0.2 m TBAI produced a 3:1 mixture of 2-methyl-1,2,3,4-tetrahydronaphthalene and 6-methyl-1,2,3,4-tetrahydronaphthalene together with a small amount (~ 1 %) of some compound(s) with $m/e = 202$, assumed to be butylated methyltetrahydronaphthalene. The low yield of butylated compounds is not surprising in view of the finding,[4] that the coupling reaction (5) competes much less effectively with the electron transfer reaction for $B = n-C_4H_9$ than it does when $B = t-C_4H_9$.

The reductive alkylation of an aromatic hydrocarbon, such as 2-methylnaphthalene, by

a radical mechanism (5) suggests thus the electron transfer in solution between the 2-methylnaphthalene anion radical (or possibly through participation of the dianion) and the tetrabutylammonium ion. It would be of interest to investigate whether this reaction effectively blocked an electron transfer to another BX-compound, which was reduced at so negative a potential that it did not give a wave at the dropping mercury electrode in DMF/TBAI.

Benzyl isopropyl ether does not give a polarographic wave in DMF/TBAI; a preparative indirect reduction of benzyl isopropyl ether, using electrolytically generated 1-methylnaphthalene anion radical in DMF/TBAI, gave, however, toluene in high yield. The electron consumption corresponded to $n = 2$ for benzyl isopropyl ether and $3 < n < 4$ for 1-methylnaphthalene, which is present in a concentration less than one third of the concentration of the ether.

These results may be explained, if it is assumed, that the rate of decomposition of benzyl isopropyl ether anion radical is much faster than that of the tetrabutylammonium radical, or that the tendency of electron transfer in solution to the tetrabutylammonium ion is considerably smaller than the polarographic results suggest; probably both effects are operating with the results that the available potential region is enlarged.

In this context it does not matter whether the electron on its way from the 1-methylnaphthalene anion radical to the benzyl isopropyl ether has resided on one or more tetrabutylammonium entities as long as the tetrabutylammonium radical loses the electron again before it decomposes. The electron consumption observed does not allow the reduction of more than a very small amount TBAI. The excessive electron consumption observed in some cases [3,5] was thus not found here.

In this connection it might be mentioned that the anion radical also could have exchanged the electron with other methylnaphthalene molecules before it finally reached the benzyl isopropyl ether molecule, the anion radical of which decomposed. This possibility is open to all anion or cation radicals where the irreversible reaction of the radical ion (protonation, deprotonation, cleavage) is slow compared to the rate of electron transfer between species of the same kind; this rate, which is known from the line-

broadening in the EPR spectra,[6] is of the order of 10^8 m^{-1} s^{-1}. In the process of electron transfer in solution the heterogeneous nature of the electrode reaction is lost and perhaps such an electron transfer in solution between species of the same kind is responsible for the lack of steric influence of the electrode found in most electrolytic reactions in aprotic media.

EXPERIMENTAL

Materials. Benzyl isopropyl ether, prepared from benzyl chloride and sodium isopropylate in isopropyl alcohol, was shaken with a solution of iron(II) sulfate to remove peroxides, dried and distilled immediately before use.

Reduction of 2-chloropyridine (a). A mixture of 2-chloropyridine (0.50 g) and anthracene (0.10 g) was reduced at -2.10 V (aq. SCE) in DMF/0.1 m TBAI. The electron consumption corresponded to a 2-electron reduction of 2-chloropyridine. In the reduced solution pyridine $(84-86 \%)$ was determined by GLC on a 15 % polyethyleneglycol 4000 column at 70 °C with o-xylene as internal standard. (b) A similar reduction $(n = 2)$ was carried out at -2.08 V with 0.1 m LiCl as supporting electrolyte; yield of pyridine 85 %.

Reduction of 2-methylnaphthalene (a). 2-Methylnaphthalene (5 g) was reduced at -2.65 V (aq. SCE) in DMF/0.3 m TBAI; $n = 7.4$, which indicates reduction of other compounds besides 2-methylnaphthalene. The catholyte was diluted with water and extracted with distilled petrol ether. The organic layer was washed several times with water to remove DMF, dried and evaporated *in vacuo*. The residue was analyzed by GLC on 5 % SE 30 at 120 °C, which gave 2 major peaks, one of them corresponding to 2-methyl-1,2,3,4-tetrahydronaphthalene and the other one to 6-methyl-1,2,3,4-tetrahydronaphthalene; a minor peak at longer retention time (1 % of the major peaks) was attributed to a butylated tetrahydromethylnaphthalene due to the fact that mass spectrometry of the crude product showed peaks up to and including m/e 202 and none at higher m/e. Attempted separation of the major components by preparative GLC gave the two components in about 95 % purity; ^1H and ^{13}C NMR-spectroscopy, however, readily identified the major compounds. ^1H NMR. 2-Methyl-1,2,3,4-tetrahydronaphthalene (CCl$_4$): $\delta = 1.03$, doublet, $J = 6.5$ Hz, $\sum H = 3$; $\delta = 1-3$, series of multiplets, $\sum H = 7$; $\delta = 6.93$, singlet, $\sum H = 4$. 6-Methyl-1,2,3,4-tetrahydronaphthalene (CCl$_4$): $\delta = 1.6-1.9$, multiplet, $\sum H = 4$; $\delta = 2.20$, singlet, $\sum H = 3$; $\delta = 2.5-2.8$, multiplet, $\sum H = 4$; $\delta = 6.78$, $\sum H = 3$. The two multiplets resemble the corresponding ones of tetraline.

Indirect reduction of benzyl isopropyl ether. A mixture of 0.5 ml (0.513 g) 1-methylnaphthalene

and 2.0 ml (1.88 g) benzyl isopropyl ether in
N,N-dimethylformamide (DMF) containing 0.1
m tetrabutylammonium iodide (TBAI) was
reduced at -2.1 V vs. Ag/AgI-electrode (-2.6
V vs. aq. SCE). The solution turned green and
remained so until the reduction was finished.
The electron consumption could be accounted
for by assuming $n = 2$ for the reduction of the
ether and n between 3 and 4 for the methyl-
naphthalene. The yield of toluene was deter-
mined (93 %) directly in the reduction mixture
by GLC on a 15 % polyethylene glycol 4000
column at 80 °C with p-xylene as internal
standard.

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