Indirect Electrolysis. Reaction between Alkyl Halides and Electrolytically Generated Anion Radicals

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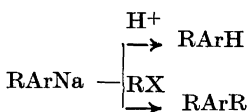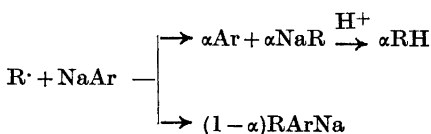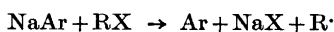
The reaction between alkyl halides and electrolytically generated anion radicals of aromatic hydrocarbons has been studied by cyclic voltammetry and controlled potential electrolysis. The results may be interpreted to show that the reaction proceeds through an electron transfer to the alkyl halide. The aliphatic radical, probably after loss of a halide ion, may react with an aromatic anion radical in two ways; the unpaired electron on each of the two reactants may form a bond between the reactants (coupling) or one electron is transferred from the aromatic anion radical to the aliphatic radical. The outcome of this competition depends on the structure of the aliphatic halide and is discussed in terms of electron affinities of the reactants. In some cases the two-electron product, the dianion, may be considered as the electron-donating species and its reaction with an alkyl halide would be of interest in connection with the mechanism of the S_N2-reaction.

From a preparative point of view, an advantage of the electrocatalytic reduction of alkyl halides is that it takes place with much less overvoltage than is required for the direct reduction at the electrode; the coupling reaction has the disadvantage that it seldom leads to a single product, but more often to a complex mixture. This disadvantage is, however, sometimes compensated by the fact that otherwise inaccessible compounds may be formed.

This paper describes an investigation on the reaction between aromatic anion radicals and aliphatic halides as a part of a more general study [1,2] of indirect reductions and oxidations by means of electrolytically generated anion and cation radicals.

The reaction between aromatic anion radicals, formed by reaction between an alkali metal and an aromatic hydrocarbon, and an alkyl halide has been the subject of many studies;[3-9] sodium dihydronaphthylide (sodium naphthalene, $NaC_{10}H_8$) has been a favoured reactant, and several types of alkyl halides, including primary alkyl fluorides,[9] have been included in these studies. The conclusion has been that the following scheme describes the reactions between alkyl halides and radicals from difficultly reducible aromatic hydrocarbons.
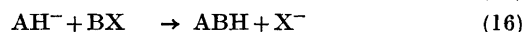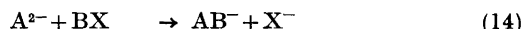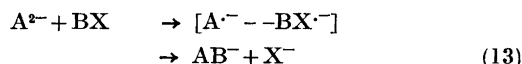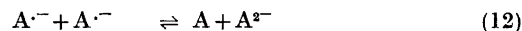
$$NaAr + RX \rightarrow Ar + NaX + R \cdot$$

$$R \cdot + NaAr \quad \overbrace{\begin{array}{l} \longrightarrow \alpha Ar + \alpha NaR \overset{H^+}{\longrightarrow} \alpha RH \\ \\ \longrightarrow (1-\alpha)RArNa \end{array}}$$

$$RArNa \quad \overbrace{\begin{array}{l} \overset{H^+}{\longrightarrow} RArH \\ \overset{RX}{\longrightarrow} RArR \end{array}}$$

The reaction between anion radicals and alkyl halides depends on many parameters, e.g. the electron affinities of the reactants, the solvent, and ion pairing.[10-12] In the present investigation N,N-dimethylformamide (DMF) has been used as solvent; as supporting electrolyte has been employed tetrabutylammonium iodide (TBAI). The ion pairing of the anion radical with the quaternary ammonium cation in DMF is much less pronounced than with lithium or sodium ions in dimethoxyethane or tetrahydrofuran.

The systems have been studied primarily by cyclic voltammetry and controlled potential electrolysis.

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RESULTS AND DISCUSSION

Catalytic reactions. The results will be discussed on the basis of the following reaction scheme, where A represents a compound forming a stable anion radical and BX is a compound forming an unstable anion radical; the reactions (1) and (7) are heterogeneous reactions involving the cathode, whereas the other reactions are homogeneous ones; (2) and (3) may be concerted.

$$A + e^- \rightleftharpoons A^{\cdot-} \tag{1}$$

$$A^{\cdot-} + BX \rightleftharpoons A + BX^{\cdot-} \tag{2}$$

$$BX^{\cdot-} \rightarrow B^{\cdot} + X^- \tag{3}$$

$$A^{\cdot-} + B^{\cdot} \rightleftharpoons A + B^- \tag{4}$$

$$A^{\cdot-} + B^{\cdot} \rightarrow AB^- \tag{5}$$

$$B^{\cdot} + B^{\cdot} \rightleftharpoons B - B \tag{6}$$

$$B^{\cdot} + e^- \rightleftharpoons B^- \tag{7}$$

$$B^{\cdot} + HS \rightleftharpoons BH + S^{\cdot} \tag{8}$$

$$B^- + H^+ \rightleftharpoons HB \tag{9}$$

$$AB^- + H^+ \rightleftharpoons ABH \tag{10}$$

$$AB^- + BX \rightarrow AB_2 + X^- \tag{11}$$

$$A^{\cdot-} + A^{\cdot-} \rightleftharpoons A + A^{2-} \tag{12}$$

$$A^{2-} + BX \rightarrow [A^{\cdot-} - -BX^{\cdot-}]$$
$$\rightarrow AB^- + X^- \tag{13}$$

$$A^{2-} + BX \rightarrow AB^- + X^- \tag{14}$$

$$A^{2-} + H^+ \rightleftharpoons AH^- \tag{15}$$

$$AH^- + BX \rightarrow ABH + X^- \tag{16}$$

$$AH^- + H^+ \rightleftharpoons AH_2 \tag{17}$$
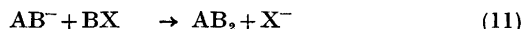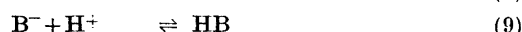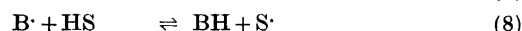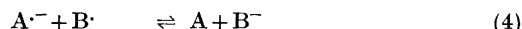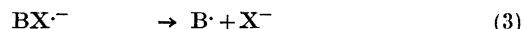
Cyclic voltammetry. The reactivities of organic halides, proton donors and olefins in DMSO towards electrochemically generated radical ions have recently been studied [13] by cyclic voltammetry, but the electrocatalytic nature of the reactions involving halides seems not to have been appreciated.

A typical electrocatalytic reaction follows (1), (2), (3), (4), and (9). In Fig. 1 is shown cyclic voltammograms of a system (phenanthrene, chlorobenzene) which follows that sequence;[1] no coupling products (5) have been isolated. From Fig. 1 it is seen that the peak-height of phenanthrene grows steadily with the concentration of chlorobenzene. Note also, that no wave appears at about − 2.6 V (aq. SCE; − 2.1 V *vs* Ag/AgI) between the first peak and that of chlorobenzene at about − 2.8 V (aq. SCE; − 2.3 V *vs* Ag/AgI), and that the oxidation wave of the anion radical disappears on addition of chlorobenzene.
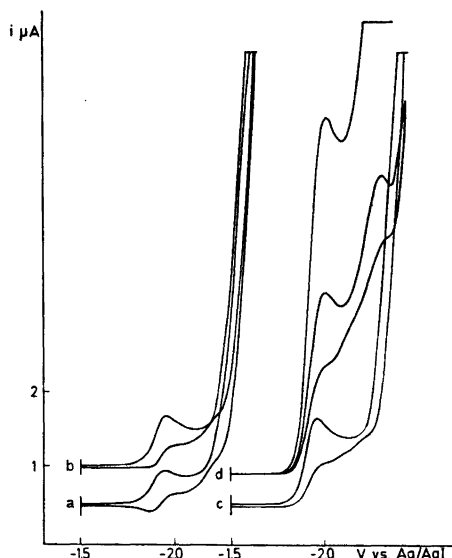

Fig. 1. Cyclic voltammograms at a stationary mercury electrode of phenanthrene (8×10^{-4} M) in presence of an increasing concentration of chlorobenzene; medium DMF/0.1 M TBAI, v = 10 mV/s. Concentration of chlorobenzene: a, 0; b, 1.2×10^{-4} M; c, 6×10^{-4} M; d, 4.8×10^{-3} M; d is shown with two sensitivities.

Cyclic voltammograms of a system, in which some coupling (5) occurs, is shown in Fig. 2, where biphenyl is studied in the presence of an increasing concentration of *tert*-butyl chloride. The following features will be discussed: The peak height of the first wave, the disappearance of the second wave and the appearance of a third wave (III) between the first and the second wave.

In contradistinction to the purely catalytic wave the height of the first peak does not continue to grow with increasing concentration of the BX compound, but reaches a limit (compare also Figs. 3 and 4). This may be explained by the occurrence of the coupling reaction (5) which removes the "catalyst" A$^{\cdot-}$ from the recycling by the formation of AB$^-$. There is a competition between (4) and (5), but when the concentration of BX is high enough all A eventually ends up as AB$^-$ (ABH), even if some of the A molecules have recycled several times.

This also explains why the second wave (the wave of A$^{\cdot-}$) disappears; the anion radical does
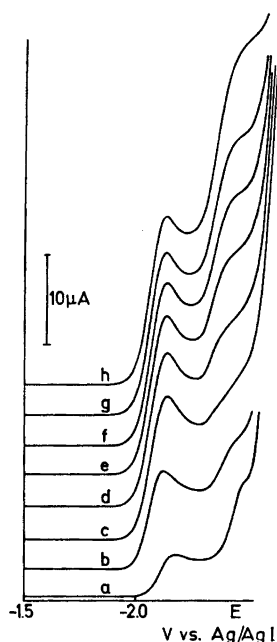
Fig. 2. Cyclic voltammograms at a stationary mercury electrode of biphenyl (5.2×10^{-3} M) with an increasing concentration of *tert*-butyl chloride; medium DMF/0.1 M TBAI; $v = 10$ mV/s. Concentration of *tert*-butyl chloride: a, 0; b, 4×10^{-3} M; c, 8×10^{-3} M; d, 1.2×10^{-2} M; e, 1.6×10^{-2} M; f, 2.0×10^{-2} M; g, 2.4×10^{-2} M; h, 2.8×10^{-2} M.

Fig. 3. Cyclic voltammograms at a stationary mercury electrode of phenanthrene (8×10^{-4} M) in the presence of an increasing concentration of *tert*-butyl chloride; medium DMF/0.1 M TBAI; $v = 10$ mV/s. Concentration of *tert*-butyl chloride: a, 0; b, 1.5×10^{-4} M; c, 7.5×10^{-4} M; d, 6×10^{-3} M.

not survive in the presence of an excess BX-compound, and there is thus no anion radical left to give the peak.

The appearance of wave III between the two original peaks may be due to the reduction of ABH, in the present case a phenylcyclohexadiene; the reduction potential of such a compound would be expected to fall at about the same potential as that of peak III. Some ABH are shown below in the preparative part, where III, VII, VIII, and XI exemplify such compounds. ABH may undergo similar reactions [(1) to (17)] as A, and as the difference in reduction potential between *tert*-butyl chloride and ABH is smaller than between biphenyl and *tert*-butyl chloride the rate of the electron exchange (2) is greater for ABH than for A. The peak heights of I and III are thus not directly comparable, and a certain peak height of III would be caused by a much smaller
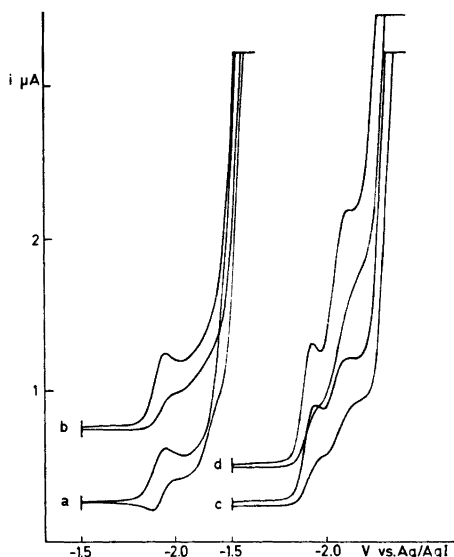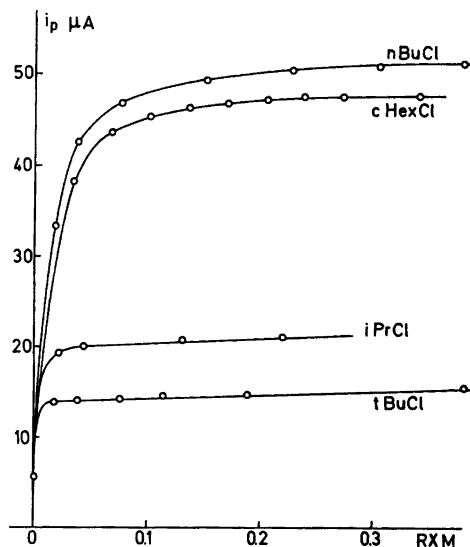

Fig. 4. Variation of the peak-height in cyclic voltammograms of naphthalene (5.5×10^{-3} M) at a stationary mercury electrode in dependence of the concentration of various halides (abscissa); medium DMF/0.1 M TBAI, $v = 10$ mV/s. The following halides were used: *tert*-butyl chloride, isopropyl chloride, cyclohexyl chloride, and butyl chloride.

concentration of ABH than would be required of A to give a similar peak height of I.

The wave III could, however, also be considered to be a prewave to the second wave in a similar way as described below for the first wave. The occurrence of this wave would then imply a fast reaction (e.g. proton abstraction, electron transfer) between the dianion and the alkyl halide.

In Fig. 3 the voltammograms of phenanthrene in the presence of tert-butyl chloride illustrates the constant peak height of wave I at higher concentrations of BX and the disappearance of wave II and the oxidation wave of A·⁻ at low concentrations of BX. The existence of coupled, partly hydrogenated products is suggested by the occurrence of a peak between I and II (the latter partly covered by the background current); peak III can be interpreted from its potential to be caused by a compound having a naphthalene or biphenyl nucleus intact.

The fact that the peak III occurs at about the same potential for BX being tert-butyl and n-butyl chloride supports the suggested explanation that peak III is caused by an ABH-compound. This, combined with a rather large difference (about 280 mV) between peak III and peak II makes it less likely that III is a "prepeak" to peak II.

When a coupling (5) takes place the peak height reaches a limit or a very slow growth on increasing the concentration of the BX-compound, the value of this limit may be interpreted as being dependent on the competition between the "catalyst-neutral" reactions [(4), (6), (7), (8)] and the "catalyst-removing" reaction, the coupling reaction (5). In Fig. 4 is depicted the dependence of the peak height of the first peak of naphthalene on the concentration of the following BX-compounds; tert-butyl chloride, isopropyl chloride, cyclohexyl chloride, and butyl chloride.

The limiting values of the peak heights depend on the structure of the BX-compound; the lower the limit the more effectively (5) competes with the other reactions. The results depicted in Fig. 4 thus predict that the current yield of coupling products with tert-butyl chloride is much higher than that for butyl chloride in the reaction with naphthalene anion radical.

This prediction was tested in the following experiment; four similar reductions of naphtha-

Table 1. Relative yields of unreacted naphthalene and coupled products in a 2 F/mol reduction of naphthalene in the presence of a 5-fold excess of alkyl chloride (BCl).

B	Naphthalene/ coupled products
Butyl	3.6
Cyclohexyl	1.35
Isopropyl	1.2
tert-Butyl	0.44

lene in DMF/TBAI were made in the presence of one of the four above mentioned aliphatic chlorides; a quantity of electricity, 2 F/mol, calculated on the basis of the concentration of the hydrocarbon, was passed and the reaction mixture analyzed by NMR after isolation of the mixture of hydrocarbons. The results, which are shown in Table 1, indicate a good yield (~70 %) of coupled product for tert-butyl chloride and a much lower yield (22 %) for butyl chloride with the secondary chlorides giving intermediate yields (40 − 45 %). Besides the radical coupling (5) the S_N2-reaction of AH⁻ (16) may be responsible for the formation of some of the butylated products. The magnitude of, e.g., the tert-butyl signals compared to the aromatic protons of the partly hydrogenated ring shows that the tert-butyl chloride has not to any appreciable degree functioned as a proton donor, as only traces, if any, of tetraline and dihydronaphthalenes could be detected in the mixture.

In the cyclic voltammetric experiments (Fig. 4) cyclohexyl chloride behaves more like butyl chloride than like isopropyl chloride, whereas in the preparative electrolysis (Table 1) the two secondary chlorides behave more alike.

These results indicate, that the ratio $R^* = i_p^1/i_p^0$, where i_p^1 is the peak height of A in the presence of high concentrations of BX and i_p^0 is the height in the absence of BX, is dependent on B. If B is aromatic or benzylic no limiting value has been observed in the concentration region employed; primary alkyl halides give a high ratio R^*, whereas tertiary alkyl halides give a low ratio, with secondary alkyl halides lying in between.

This may be rationalized on the basis of considerations on electron affinity of the reac-
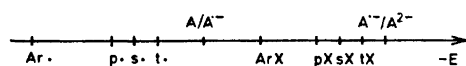
Fig. 5. Schematical representation of a possible distribution of half-wave potentials of some reactants in electron transfer reactions. ArX = aromatic halide; pX = primary aliphatic halide; sX = secondary aliphatic halide; tX = tertiary aliphatic halide; Ar·, p·, s·, t· = aromatic, primary, secondary, and tertiary aliphatic radicals, respectively.

tion partners. Only few measurements have been made on the redox potential of aliphatic radicals,[13-17] but it seems reasonable to assume the following order of electron affinity: $Ar· >$ $RCH_2· > RR'CH· > RR'R''C·$. In Fig. 5 the redox potentials of the different reaction partners are shown schematically on a potential axis. The rate of electron transfer from an aromatic anion radical to a primary alkyl radical is thus faster than the transfer to a tertiary alkyl radical. If it is also assumed, that for aliphatic radicals the rate of the coupling reaction (5) is less dependent on structure than (4), it follows that the coupling reaction would be favoured for tertiary alkyl halides compared to primary ones.

The ratio R^* (i_p^1/i_p^0) is, for a given BX compound, independent of the concentration of A as shown in Fig. 6. Further experiments are
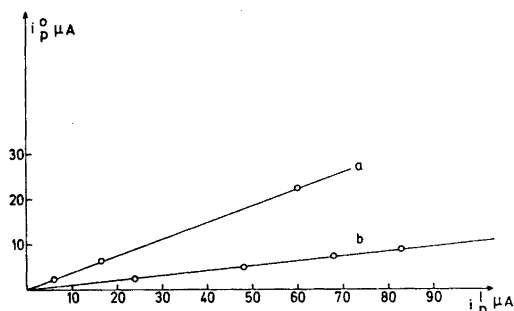

Fig. 6. Cyclic voltammetric results of different concentrations of naphthalene at a stationary mercury electrode in presence of an excess of alkyl halide. Medium: DMF/0.1 M TBAI; scan rate 10 mV/s. Ordinate: Peak currents of naphthalene at different concentrations; abscissa: Peak currents of naphthalene at the same concentrations in presence of excess of the following halides: a, *tert*-butyl chloride; b, butyl chloride.

planned to elucidate the influence of solvent, temperature, and other parameters on the ratio R^*. From the concentration independence of R^* it seems likely that the second order dimerization (6) is less important for the fate of B· than the electron exchange reaction (4).

If the competition between (4) and (5) is the deciding factor for R^*, then the reactants A·⁻ and B· react with each other in such a way that a constant product ratio occurs. A possible interpretation of this is, that the radical reactants form a complex, in which there is a constant probability for the two unpaired electrons either to form a bond (5) or to be localized at one of the reactants (4). The concept of a complex seems attractive, but the available data cannot exclude other interpretations.

In Fig. 7 is shown the dependence of the ratio R^* on the peak potential (easily related to the redox potential) of the aromatic A-compound; *tert*-butyl chloride, isopropyl chloride and butyl chloride are included as BX-compounds. The trend of the data is clear, the more negative the redox potential, the higher is the ratio R^*, in accordance with the explanation, that a high value of R^* is the result of a high rate of an electron exchange reaction.

In Fig. 8 are shown cyclic voltammograms of *trans*-stilbene in the presence of an increasing concentration of *tert*-butyl bromide. *trans*-Stilbene alone gives two one-electron steps of which the first one is reversible. On addition of a small amount of *tert*-butyl bromide a prepeak appears; the peak height of the second peak of stilbene decreases and so does the anodic peak of the reoxidation of the stilbene anion radical. On further addition of *tert*-butyl bromide these trends continue until the prepeak and the first peak of stilbene merge, and the second one-electron step and the anodic one disappear completely. This happens at a concentration of *tert*-butyl bromide which is considerably smaller than that necessary for reaching the limiting value of the peak height.

Such a prepeak could be observed if a species, more easily reduced than the A-compound, were formed in a fast follow-up reaction (or reactions) of the anion radical A·⁻. In the present case such reactions could be (2) and (3) with formation of the easily reducible radical B·. Electron transfer to this radical and/or the re-formed A would be responsible for the observed prepeak,
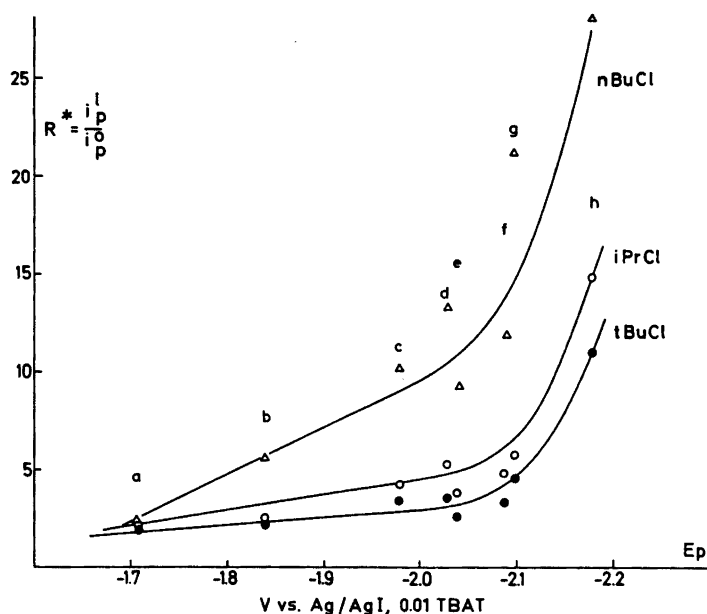
Fig. 7. Dependence of the ratio $R^* = i_p^l / i_p^0$ of different A-compounds on their peak-potentials for different aliphatic halides in DMF/TBAI, a, *trans* stilbene; b, *p*-terphenyl; c, phenanthrene; d, 1-methylnaphthalene; e, naphthalene; f, 2-methylnaphthalene; g, biphenyl; h, acenaphthene. Aliphatic halides: Butyl chloride; isopropyl chloride; *tert*-butyl chloride.

the height of which would be limited by the concentration of BX.

The prepeak could, however, also be formed by a mechanism akin to the one observed during the anodic pyridination of 9-phenylanthracene; such prepeaks were studied by means of simulation technique.[18] It was found that a prepeak could be obtained as well in an *ece*-reaction as in an *ecec*-reaction (electron transfer − chemical reaction − electron transfer − chem-
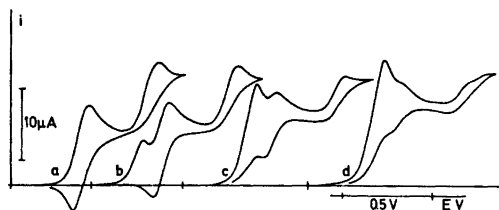

Fig. 8. Cyclic voltammograms at a stationary mercury electrode of *trans*-stilbene (5.1×10^{-3} M) in DMF/0.1 M TBAI containing different concentrations of *tert*-butyl bromide. Starting potential − 1.3 V *vs.* Ag/AgI; sweep rate 10 mV/s. Concentration of *tert*-butyl bromide: a, 0; b, 3.5×10^{-3} M; c, 1.08×10^{-2} M; d, 1.5×10^{-2} M.

ical reaction), provided certain parameters were of the right magnitude and certain conditions met. The prepeak depended on many factors such as the rate constants of the reactions involved, the concentrations of the reacting molecules, their diffusion coefficients, and the sweep rate. The essential feature of the phenomenon in a cathodic process is that there in the reaction scheme is a rapid, practically irreversible reaction which removes the reduced product; the removal of the reduction product induces a further reduction of the substrate in order to retain the concentration ratio required by the Nernst equation. The reduction thus occurs at a less negative potential than in the reversible case. Both reactants are removed in the irreversible reaction, and the height of the prepeak is limited by the depletion of the reactant present in lowest concentration. In the present case the peak height might be limited by the concentration of the B-radical, which in turn is dependent on, among other things, the BX-concentration.

A prewave has not been observed for aromatic BX-compounds; aromatic B-radicals do not
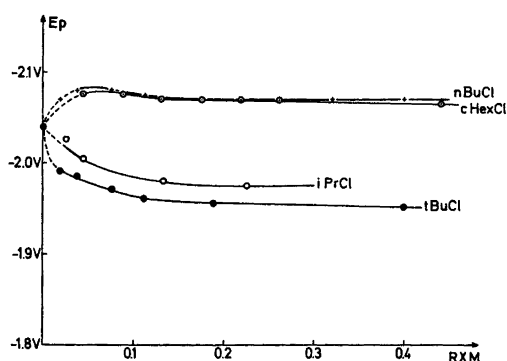
Fig. 9. Dependence of the peak potential of the first wave of naphthalene on the concentration of the following aliphatic halides: tert-butyl chloride, isopropyl chloride, cyclohexyl chloride, and butyl chloride.

couple with $A^{\cdot-}$. For aromatic BX-compounds the reaction sequence (1), (2), (3), (4) is followed, and the reaction responsible for the prepeak cannot be sought among these reactions. Aliphatic BX-compounds couple to a higher or lower degree (5). If thus (2) and (4) behave reversibly in this context and (5) for all practical purposes behave irreversibly, the occurrence of the prepeak in the present case could be explained in a way akin to that employed for the voltammetric pyridination of 9-phenyl-anthracene.[18]

In Fig. 9 is shown the dependence of the peak potential of the first wave of naphthalene in dependence of the concentration of tert-butyl chloride, isopropyl chloride, cyclohexyl chloride, and butyl chloride. The halides, which are assumed (Fig. 4, Table 1) to give a high current yield of coupling products, shift the peak potentials to more positive potentials, whereas a slight shift to more negative values is observed in the presence of good electron acceptors, such as aromatic BX-compounds and, to a lesser degree, butyl chloride.

The positive shift of the peak potential has the same background as the prewave, as it is due to an irreversible process which removes the reduced product, thereby bringing about a further reduction of the substrate in order to retain the concentration ratio required by the Nernst equation. When the prepeak merges with the original peak the positive shift is observed. However, as a purely catalytic peak is shifted [19]

to more negative potentials on increasing the concentration of BX, there are at least two opposing factors operating. If the coupling reaction dominates, a positive shift is found, but when the electron exchange dominates, a shift to more negative potentials is observed.

In some cases electron-transfer from a dianion A^{2-} of an aromatic compound to a BX-compound may be possible.[20] Addition of highly active alumina to DMF removes proton donors and makes it possible to observe two reversible one-electron steps for many compounds;[21] using that technique the reaction between A^{2-} and BX has been studied.[22] The dianions are much stronger bases (and nucleophiles) than the anion radicals; perylene dianion thus exchanges electrons with dichlorobenzene, but its reaction with butyl chloride is a proton abstraction or substitution reaction rather than an electron exchange reaction involving a catalytic reduction of butyl chloride. In this connection it could also be mentioned that a reaction with the dianion is only observed when the reaction between $A^{\cdot-}$ and BX is so slow that BX is not preferentially removed by this reaction.

For compounds forming less basic dianions or where ion-pairing diminishes the tendency to proton abstraction the two-electron reduction product may undergo electron exchange with a suitable aliphatic BX-compound. The reaction of a dianion with a BX-compound could be formulated as a classical S_N2-reaction (transfer of two electrons simultaneously) or as an electron exchange resulting in two anion radicals, which then could couple; the coupling could possibly be between $A^{\cdot-}$ and $B^{\cdot}$, the latter formed by decomposition of $BX^{\cdot-}$. The S_N2 reaction has been shown to proceed in certain cases [23,24] via a primary electron exchange; experiments with other types of substrates than used here are in progress to investigate the possible use of electrochemical methods in elucidating certain aspects of the S_N2 reaction.

The results from the cyclic voltammetric investigation are in agreement with the findings by earlier methods [3-9] that the coupling between an anion radical from an aromatic hydrocarbon ($A^{\cdot-}$) and an alkyl halide occurs between $A^{\cdot-}$ and the aliphatic radical $B^{\cdot}$. The cyclic voltammetric data often makes it possible to foretell the relative importance of the possible reactions; sometimes merely the reduction potentials of

the reactants involved may suffice, but often a proper cyclic voltammetric investigation is needed to make a prediction.

Preparative electrolysis. The preparative electrolysis of the systems described in this investigation has two aspects, the catalytic reduction [25,26] and the reductive coupling reaction. The catalytic reduction of an alkyl halide by means of an anion radical can be performed at a much less negative potential than that required by a direct reduction at the electrode; in effect, the overvoltage is drastically reduced. The electron transfer between an aromatic anion radical and an aliphatic alkyl halide (possibly within a collision complex) is thus not inhibited by a similar high reaction barrier as the heterogeneous electron transfer between the mercury electrode and the alkyl halide. The activation energy in the reduction of alkyl chlorides at a vitreous carbon electrode [27] seems to be smaller than that connected with the reduction at a mercury electrode, but both of the heterogeneous reactions mentioned have apparently larger activation energies than the homogeneous reaction. Possibly the electrode does not act only as an electron source; the electrode material may play a role in the process.

Besides aliphatic hydrocarbons, preparative electrolysis of aromatic hydrocarbons in the presence of an alkyl halide gives, in general, rise to the formation of alkylated, partly hydrogenated compounds. Some examples will be mentioned.

Reduction of stilbene in DMF/TBAI in the presence of *tert*-butyl chloride at −2.3 V (aq.
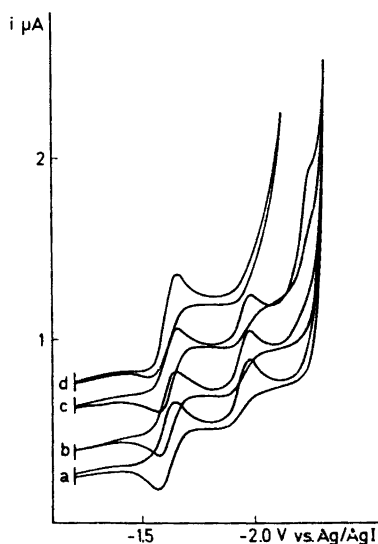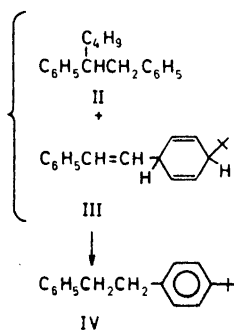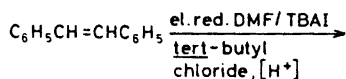
$$C_6H_5CH=CHC_6H_5 \xrightarrow[\substack{tert-butyl \\ chloride,[H^+]}]{el.red.DMF/TBAI}$$

$$
\left\{
\begin{array}{c}
\underset{II}{\overset{\displaystyle C_4H_9}{C_6H_5\overset{|}{C}HCH_2C_6H_5}} \\[2em]
+ \\[1em]
\underset{III}{C_6H_5CH=CH\diagdown\!\!\!\!\diagup}
\end{array}
\right.
$$

$$C_6H_5CH_2CH_2\!\!-\!\!\diagup\!\!\!\!\!\bigcirc\!\!\!\!\!\diagdown\!\!+$$

IV

Fig. 10. Cyclic voltammograms at a stationary mercury electrode of *trans*-stilbene (7.5×10^{-4}M) in presence of different concentrations of *tert*-butyl chloride; medium DMF/0.1 M TBAI, $v = 10$ mV/s. Concentrations of *tert*-butyl chloride: a, 0; b, 1.5×10^{-4} M; c, 7.5×10^{-4} M; d, 1.2×10^{-3} M.

SCE) yielded a 3:2 mixture of the known [28] 3,3-dimethyl-1,2-diphenylbutane (II) and the hitherto unreported 1-phenyl-2-(4′-*tert*-butylphenyl)ethane (IV). No dialkylated products were observed; presumably the anion [AB⁻, reaction (5)] would rather abstract a proton than react with *tert*-butyl chloride in a substitution reaction.

III is assumed to be an intermediate on the basis of the cyclic voltammetric curves (Fig. 10); these indicate the formation of a compound which is reducible just prior to the reduction of TBAI. As neither II nor IV are reducible at that potential, the styrene derivative III has been suggested here as the compound responsible for that wave.

Reduction of naphthalene under similar conditions gave a reaction mixture which unsuccessfully was sought separated by preparative GLC. Only one fraction was sufficiently pure for identification by ¹H NMR; the others contained three or more compounds. By ¹³C NMR the mixtures could be analyzed, and the following products were found and characterized by their ¹³C NMR-spectra:

$$C_{10}H_8 \xrightarrow[\substack{tert\text{-butyl} \\ \text{chloride,}[H^+]}]{\text{el.red.DMF/ TBAI}}$$
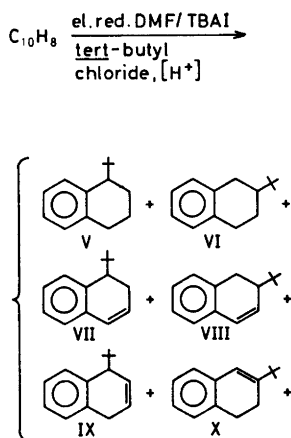
The coupling products formed are probably primarily the difficultly reducible 1,4-dihydronaphthalenes; these tautomerize under influence of the base created at the cathode into the 1,2- or 3,4-dihydro derivative which is reducible at a potential about 0.2 V more negative than that of naphthalene. These dihydronaphthalenes are thus examples of ABH-compounds suggested above to be responsible for the occurrence of the so-called wave III in the cyclic voltammetric experiments. Possibly some isomerization occurs during the work-up. The reaction mixture was aromatized by treatment with sulfur and the resulting products consisted of a 1:3 mixture of 1- and 2-tert-butylnaphthalene.

Anthracene produced on reduction in presence of methyl chloride mono- and dimethylated dihydroanthracenes. On column chromatography only one of the minor components was separated from the major components, which from the ¹H NMR-spectrum and mass spectrum seemed to be mainly a mixture of 9-methyl- and 9,10-dimethyl-9,10-dihydroanthracenes. The isolated minor component was 2-methyl-1,2-dihydroanthracene (XI), which is another example of a reducible ABH-compound.

The dialkylated compounds may be formed in a classical S_N2-reaction (11) between AB^-, formed in (5), and alkyl chloride.

Reduction of anthracene in the presence of

XI
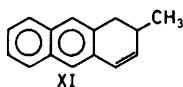
tert-butyl chloride yielded much more products alkylated in the 1- and 2-positions (60 %) than did the reaction with methyl chloride. Steric factors may be responsible for the lowered tendency of the tert-butyl radicals to attack the 9-position.

From a preparative point of view such reactions are not attractive due to the complexity of the reaction mixtures formed; however, this complexity makes it probable, that many of the possible isomers are present in the mixture, and if the separation problem can be solved, the reaction may be used to prepare otherwise inaccessible compounds. 1-tert-Butylpyrene, which has been sought prepared in several conventional ways without success, is thus the main product on electrolytic reduction of pyrene in DMF/TBAI in the presence of tert-butyl chloride.[29]

EXPERIMENTAL

Apparatus. For electrolysis and cyclic voltammetry was used apparatus previously described;[30] a Hewlett Packard 7045A $x-y$ recorder was used for recording the cyclic voltammograms.

Reduction of anthracene. Anthracene (1 g) was reduced in DMF/TBAI at -2.0 V (SCE) in the presence of methyl chloride, $n=7-10$. The reduction completed, the DMF was removed *in vacuo*, the residue treated with water and diethyl ether, and the ether layer washed three times with water. After drying the ether was evaporated; ¹H NMR of the residue suggested a mixture of mono- and dimethylated 9,10-dihydroanthracenes (85 %) and about 15 % 1- or 2-methyldihydroanthracene. Attempted separation of the mixture by column chromatography on silica with light petroleum as eluent met only limited success, as only one of the components was separated from the remaining mixture, this compound was identified as 2-methyl-1,2-dihydroanthracene from the ¹H NMR-spectrum (CDCl₃): δ 1.06 (d, 3 H, J 6.5 Hz), 2.0−3.3 (m, 3 H), 5.91 (pair of d, 1 H, J_1 10 Hz, J_2 2.7 Hz), 6.55 (broadened d, 1 H, J_1 10 Hz, $J_2 \sim 1$ Hz), 7.1−7.9 (m, 6 H).

Reduction of anthracene under similar conditions with tert-butyl chloride replacing methyl chloride gave a different product distribution ($n=1.9$), as compounds alkylated in the 1- or 2-positions were responsible for about 60 % of the reaction mixture. This estimation was made on basis of a comparison of the integration of the protons in the region of ethylenic protons with that of the aromatic and aliphatic protons.

Reduction of stilbene and tert-butyl chloride. trans-Stilbene (1 g) was reduced at -2.3 V (aq.

SCE) in DMF/0.1 m TBAI in the presence of 10 ml *tert*-butyl chloride. The solution turned green, fading at the end of the reduction, $n = 2.6$ F/mol; the n-value indicates a low degree of catalytic reduction of *tert*-butyl chloride. The reduction completed, most of the DMF was removed *in vacuo*, the remnant treated twice with water and distilled light petroleum. The light petroleum was washed with water, dried and evaporated. The ^{1}H NMR-spectrum indicated a mixture of approximately 60 % 3,3-dimethyl-1,2-diphenylbutane and 40 % 1-phenyl-2-(4'-*tert*-butylphenyl)ethane. The mixture was separated by preparative GLC on a 15 % SE 30 at a programmed column temperature 100 to 210 °C and a flow rate of 200 ml/min. The fractions were recrystallized from a small volume of ethanol and sublimed. 3,3-Dimethyl-1,2-diphenylbutane, m.p. 40 °C $(36 - 37.5$ °C);[28] ^{1}H NMR-spectrum $(CDCl_3)$: δ 0.95 (s, 9 H), $2.5 - 3.3$ (m, 3 H), $6.9 - 7.2$ (m, 10 H). (Found: C 90.75; H 9.26. Calc. for $C_{18}H_{22}$: C 90.70; H 9.30). 1-Phenyl-2-(4-*tert*-butylphenyl)ethane, m.p. 45 °C; ^{1}H NMR-spectrum $(CDCl_3)$: δ 1.30 (s, 9 H), 2.89 (s, 4 H) $7 - 7.4$ (m, 9 H). (Found: C 90.49; H 9.22. Calc. for $C_{18}H_{22}$: C 90.70; H 9.30).

Reduction of naphthalene (1). 1 g of naphthalene was reduced in DMF/TBAI in the presence of excess BX [(a) 10 ml *tert*-butyl chloride; (b) 10 ml butyl chloride; (c) 12 ml cyclohexyl chloride; (d) 8 ml isopropyl chloride]; 2 F/mol naphthalene were passed using a constant current of 2.5 mA/cm². The solvent was removed *in vacuo*, and water and distilled light petroleum added to the residue. The organic layer was washed 3 times with water, dried, the solvent evaporated, and the residue analyzed by ^{1}H NMR $(CDCl_3)$. (a) δ $0.85 - 0.95$ (two main s, 9 H) $1.8 - 2.3$ (m, 3 H), $5.8 - 6.65$ (two sets of m, 2 H), $7.0 - 7.2$ (two main s, 4 H, dihydronaphthalenes) $7.3 - 7.9$ (two sets of m, 8 H, naphthalene). Yield of coupling products 70 %. The results reported in Table 1 are evaluated in a similar way.

Reduction of naphthalene (2). Naphthalene (2 g) was reduced in DMF/TBAI at -2.5 V (aq. SCE) in the presence of 10 ml *tert*-butyl chloride, $n = 3.3$ F/mol. The catholyte was diluted with water, acidified with a small volume of hydrochloric acid, and extracted with light petroleum twice. The organic layer was washed three times with water, dried, and the solvent removed *in vacuo*, residue 2.5 g. The residue was separated in three fractions by preparative GLC on a 15 % SE 30 at a column temperature of 140 °C with a flow of 120 ml/min. The components (V to X) in the fractions were identified by ^{13}C NMR.[31]

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