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Electrogenerated Anions as Electron Transfer Reagents

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The anion (1^-) generated from 1-ethyl-4-methoxycarbonyl pyridinium iodide (1^+) by electrochemical reduction has been shown to reduce 1,2-dichloro-1,2-diphenylethane by electron transfer. Reaction of 1^- with *t*-butyl bromide or 2-bromooctane leads to alkylated dihydropyridines; it is proposed that an SET mechanism is involved. Carbon dioxide also reacts with 1^- to form a dihydropyridine.

Reactions involving electron transfer in solution (SET) from anions to suitable substrates are well-known. The aromatic nucleophilic substitution reaction S_RN1 is[1-3] initiated by such an electron transfer, and the reaction of certain *p*-nitrobenzyl halides with some nucleophiles,[4-5] also involves an SET mechanism. Electron transfer is also essential for the reaction of a number of addition reactions of organometallic compounds.[6-8]

Electron transfer from electrogenerated anion radicals or dianions of aromatic, heteroaromatic and olefinic compounds (A) to suitable substrates has been reported;[9] several kinds of substrates (BX) have been employed; aromatic and benzylic halides were reduced to hydrocarbons,[10] whereas coupling products generally are obtained from aliphatic BX-compounds.[11] Anion radicals have been shown to be more efficient electron donors in a photo-excited state than in the ground state.[12]

This communication is concerned with examples of SET from electrogenerated anions to some substrates; the products of the coupling reactions are formally the same as would have been obtained by a classical nucleophilic substitution reaction.

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RESULTS AND DISCUSSION

Electrogenerated anions may be formed by reduction of a positively charged species or by a suitable cleavage reaction. Here the anion obtained by reduction of 1-ethyl-4-methoxycarbonylpyridinium iodide (1^+) is employed; the electrochemistry of 1^+ has been studied recently.[13]

In Fig. 1 are shown cyclic voltammograms of 1^+ and 1,2-dichloro-1,2-diphenylethane (*2*) and of 1^+ in the presence of *2*; the medium is *N*,*N*-dimethylformamide (DMF) with tetrabutylammonium iodide (TBAI) as supporting electrolyte. 1^+ exhibits two reversible one-electron waves, whereas *2* shows an irreversible wave followed by a reversible one due to the stilbene formed by reductive elimination;[9] both waves of *2* are found at potentials more negative than the second wave of 1^+.

Addition of *2* to a solution of 1^+ results (Fig. 1, c) in an enhancement of the second peak of 1^+ and the disappearance of the first peak of *2*. *2* is thus reduced to stilbene (*3*) by the anion 1^-, which thereby is oxidized to the radical $1^{\cdot}$. This is confirmed by an EPR experiment; *2* is added to a solution of 1^-; the EPR spectrum of $1^{\cdot}$ is obtained immediately after the addition and the intensity of the lines remains constant for several hours even in the presence of an excess of *2*.

Cyclic voltammetry of 1^+ in the presence of *t*-butyl bromide (*4*) shows a reversible wave followed by an irreversible one. The height of the second wave is not influenced by addition of *4*. Preparative reduction of 1^+ at the potential of the second wave in the presence

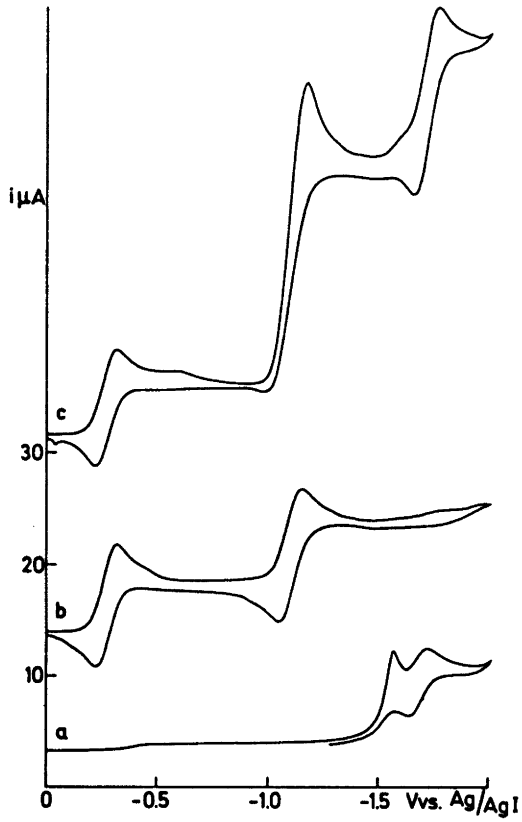
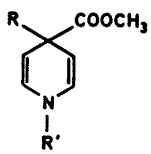


Fig. 1. Cyclic voltammograms at a platinum electrode in DMF/TBAI; potentials *vs.* Ag/AgI, 0.1 M I^--reference electrode; $v = 20$ mV s^{-1}. a: 1.9×10^{-2} M 1,2-dichloro-1,2-diphenylethane (*2*); b: 3.0×10^{-2} M 1-ethyl-4-methoxycarbonylpyridinium iodide (1^+); c: 5.6×10^{-2} M *2* + 3.0×10^{-2} M 1^+.

of *4* yielded 4-*t*-butyl-1,4-dihydro-1-ethyl-4-methoxycarbonylpyridine (*5a*) as the only isolated product.

$1^{\cdot}$ does not react with *4* as the EPR spectrum of $1^{\cdot}$ does not diminish in intensity for several hours in the presence of *4*.



5a, R = *t*-Bu, R′ = C_2H_5; *5b*, R = *sec*-octyl, R′ = CH_3; *5c*, R = $COOCH_3$, R′ = C_2H_5.

Cyclic voltammetry of 1^+ in the presence of a secondary alkyl bromide, such as 2-bromooctane (*6*), shows that the first wave remains unchanged whereas the second wave becomes irreversible and increases 30 % in the peak height. Preparative reduction of 1^+ at the potential of the second wave in the presence of *6* results in *5b* in good yield.

Addition of carbon dioxide (*7*) to a solution of 1^+ changes the cyclic voltammetric behaviour; the first wave is not affected, whereas the second one is shifted 150 mV anodically, but is still reversible. Preparative reduction of 1^+ in the presence of *7*, followed by methylation produced *5c*.

The experimental results may be explained from the general scheme:

$$A^+ + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^{\cdot} \qquad (1)$$

$$A^{\cdot} + e^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A^- \qquad (2)$$

$$A^- + BX \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A^{\cdot} + BX^{\cdot -} \qquad (3)$$

$$BX^{\cdot -} \xrightarrow{k_4} B^{\cdot} + X^- \qquad (4)$$

$$A^{\cdot} + B^{\cdot} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} AB \qquad (5)$$

$$A^- + B^{\cdot} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} AB^{\cdot -} \qquad (6)$$

$$AB^{\cdot -} + A^{\cdot} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} AB + A^- \qquad (7)$$

$$B^{\cdot} + e^- \rightleftharpoons B^- \text{ and/or} \qquad (8a)$$

$$B^{\cdot} + A^- \rightleftharpoons B^- + A^{\cdot} \qquad (8b)$$

$$B^- \longrightarrow \text{further reactions} \qquad (9)$$

When $A^+ = 1^+$ and BX = *2* the reaction sequence is (1), (2), (3), (4), (8), (9), where (9) is an E2-like elimination of Cl^- producing stilbene. Although the equilibrium of (3) is well to the left, as $1^{\cdot}$ is more easily reducible than *2*, the fast follow-up reactions (4) and (8) are a sufficient driving force for (3) to proceed to the right. When BX is *4* the product, AB (*5a*), is the same as normally would have been formed through a classical nucleophilic substitu-

tion of 1^- on *4*. An S_N2 substitution of 1^- on *4* is very unlikely for steric reasons and the finding that the anion (8^-) obtained from 4-benzoyl-1-methylpyridinium iodide (8^+) by two one-electron reductions reacts with *t*-butyl dimethylsulfonium iodide (*9*) [14] with the formation of 4-benzoyl-4-*t*-butyl-1,4-dihydro-1-methylpyridine rather than the 4-methyl analogue excludes an S_N2 reaction in the reaction between 8^- and *9*; furthermore, iodide (from TBAI) does not react with *4* in DMF at 25 °C which indicates a low reactivity of *4* in both S_N2 and S_N1 reactions.

An SET mechanism is thus an alternative; an estimate of the likelihood of such a reaction depends on a knowledge of certain parameters, *i.a.* the redox potentials of the compounds. The reversible potential $1^{\cdot}/1^-$ is measurable ($E^\circ = -1.08$ V *vs.* Ag/AgI) but that of *4* is more dubious. The peak potential of *4* is not a valid measure of that; the picture is complicated both by a fast follow-up reaction (cleavage of the carbon-bromine bond) and a low exchange current. The follow-up reaction affects the peak potential in the anodic direction whereas a low exchange current does the opposite.

The invalidity of the peak potential as a measure of the redox potential is demonstrated by the peak potentials of *4* and *6* measured at different electrodes (Table 1). In the case $1^+ + 6$ there is an enhancement of the second wave of 1^+ indicating that here the SET mechanism is operating. As the peak potential of *6* at all electrodes is more negative than that of *4* it seems reasonable that the SET mechanism is also operating in the case $1^+ + 4$; the absence of a catalytic wave of $1^{\cdot}$ may be explained by different possibilities for the radicals of *4* and *6* to escape from a radical-cage initially formed;[8] this is confirmed by a report [11] where it was found that a tertiary halide couples more efficiently with the anion radical of naphthalene than a secondary halide.

Table 1. Peak potentials (V *vs.* Ag/AgI, 0.1 M I^-) for *t*-butyl bromide (*4*) and 2-bromooctane (*6*); scan rate 40 mV s^{-1}.

	Pt	Hg	Vitreous carbon
4	−2.30	−1.90	−1.62
6	−2.40	−2.14	−1.73

If the redox potential of BX is less than half a volt more negative than $E_{\frac{1}{2}}$ of 1^-, then the rate of the overall reaction is compatible with an SET mechanism. If, however, the difference is more than half a volt, then a model which lies between an SET model and an S_N2 model and in which an electron transfer to BX is concerted with the cleavage of the carbon-halide bond might be considered. In such a model the stereochemistry might depend on, besides the redox potentials, the strength of the carbon-halide bond; chlorides would give more inversion than iodides, which would tend to give razemization. In general, a large difference between the oxidation potential of the anion (E_{A^-}) and the reduction potential of the electrophile (E_{BX}) would favour an S_N2 reaction, a small difference (E_{A^-} could even be more negative than E_{BX}) would favour the SET mechanism, and in an intermediate region a hybrid model could operate (the SET model and the S_N2 model could be regarded as extremes of the hybrid model).

The shift in the peak potential of the second peak of 1^+ in the presence of CO_2 is not caused by a fast carboxylation at C-4, as the reversibility then would have been lost; there is, possibly, a charge-transfer complex reversibly formed involving CO_2 and the basic nitrogen of $1^{\cdot}$. The mechanism of the coupling reaction is not clear.

EXPERIMENTAL

Apparatus. The equipment used for electrolysis and cyclic voltammetry has been described previously.[15] The EPR spectrometer was a Varian E-3.

Reduction of 1^+ (a). 1^+ (3 g) was reduced in DMF/0.1 M TBAI at −1.5 V (*vs.* Ag/AgI, 0.1 MI^-; −2.0 V *vs.* SCE), $n = 3.4$ F mol^{-1}. After completion of the electrolysis the catholyte was diluted with water and the product extracted with diethyl ether. The ether was washed with water, dried and evaporated leaving a residue, 1.52 g (67 %); TLC and ^1H NMR spectroscopy of the crude product indicated only one compound. The residue was recrystallized from light petroleum; m.p. 48.2–48.6 °C. The compound was identified as 4-*t*-butyl-1,4-dihydro-1-ethyl-4-methoxycarbonylpyridine from the ^1H NMR spectrum ($CDCl_3$): δ 0.85 (s, 9H); 1.08 (t, J 7.0 Hz, 3H); 3.10 (q, J 7.0 Hz, 2H); 3.65 (s, 3H); 4.75 (d, J 8.2 Hz,

2H); 5.98 (d, 8.2 Hz, 2H). The compound is stable even in the presence of air.

Reduction of 4-methoxycarbonyl-1-methylpyridium iodide (9⁺) (b). 9^+ (2 g) was reduced as 1^+ in the presence of 10 ml of 2-bromooctane (*6*), $n = 2.0$ F mol^{-1}. After work-up as described for 1^+, the excess of *6* was separated from the product on a column of silica with light petroleum as eluent. The product (1.24 g, 68 %) was identified as *5b* from the ^{1}H NMR spectrum ($CDCl_3$): δ 0.6 – 1.5 (m, 17H); 2.85 (s, 3H); 3.67 (s, 3H); 4.40 (d, 8.0 Hz, 2H); 5.92 (d, 8.0 Hz, 2H).

Reduction of 1^+ and CO_2 (c). 1^+ (1 g) was reduced as described above with bubbling of CO_2 through the catholyte. After completion of the reduction methyl chloride was bubbled through the catholyte which was allowed to stand until the next day. It was worked up as described above (a); isolated was 0.315 g (41 %) 4,4-bis(methoxycarbonyl)-1,4-dihydro-1-ethylpyridine (*5c*), light oil, which slowly decomposes on contact with air. ^{1}H NMR spectrum ($CDCl_3$): δ 1.10 (t, J 7.0 Hz, 3H); 3.15 (q, 7.0 Hz, 2H); 3.72 (s, 6H); 4.70 (d, 8.0 Hz, 2H); 6.07 (d, 8.0 Hz, 2H).

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