Indirect Electrochemical Reduction of *meso-* and *d,l*-1,2-Dichloro-1,2-diphenylethane

Torben Lund,[a] Steen U. Pedersen,[a] Henning Lund,[a,*] Kwai Ming Cheung[b] and James H. P. Utley[b]

[a]Department of Organic Chemistry, University of Aarhus, DK-8000 Århus C, Denmark and [b]Department of Chemistry, Queen Mary College, University of London, London E1 4NS, England

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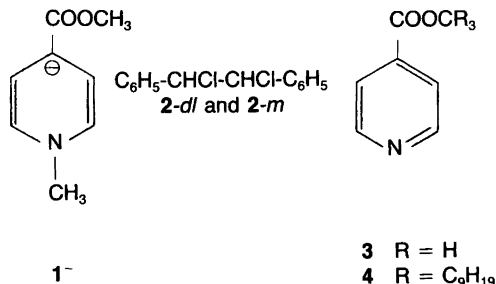
The reaction between a number of anion radicals and *d,l*- and *meso*-1,2-dichloro-1,2-diphenylethane has been shown to be a purely catalytic reduction, and the rates of the electron transfer have been measured. One catalyst, 10-nonyl-10-nonadecyl isonicotinoate, was expected to interact with the substrate via lipophilic forces, but only a small and unattributable enhancement of the electron-transfer rate was measured. The reductive elimination of halide from the *vic*-dichlorides by the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine is also purely catalytic, and it proceeds at the rate expected for the outer-sphere transfer of a single electron.

Electrodes have been modified chemically in many ways and for different purposes;[1,2] one goal is to enhance the rate of heterogeneous electron transfer, and the binding of suitable redox systems to the electrode surface has been widely employed to promote the electron exchange.
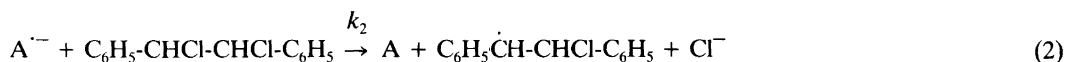
It has also been shown[3] that the cathodic cleavage of benzyl acetate and benzyl formate is catalysed when the latter compounds are included in guest-host complexes formed with β-cyclodextrin derivatised with an electrophore capable of acting as a redox catalyst. In these cases, the distinction between covalent catalysis and a mechanism involving electron transfer between host and guest has not yet been established. However, the possibility of such "intra-complex" electron transfer suggests that redox catalysts might be designed in which complexation may not be as well defined as in the cyclodextrin systems. Electron transfer might be expected to be enhanced should the mediator interact with the substrate, e.g. by "solvation" of an organic substrate by a hydrophobic (lipophilic) mediator. In terms of the ac-

cepted mechanisms for redox catalysis, the interaction would be advantageous in possibly reducing the average distance over which electron exchange takes place and prolonging the contact time for such exchange; another way of viev..ing this is that k_2 in Scheme 1 would be permitted to exceed the rate of diffusion.

To test such a possibility the rates of the electron transfer to *d,l*- and *meso*-1,2-dichloro-1,2-diphenylethane (**2-***dl*, **2-***m*) from a number of anion radicals, including the anion radicals of methyl isonicotinoate (**3**) and 10-nonyl-10-nonadecyl isonicotinoate (**4**), were measured by cyc-

COOCH₃ ... C₆H₅-CHCl-CHCl-C₆H₅ (2-*dl* and 2-*m*) ... COOCR₃

1⁻

3 R = H
4 R = C₉H₁₉

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*To whom correspondence should be addressed.

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

$$A^{\cdot-} + C_6H_5\text{-CHCl-CHCl-}C_6H_5 \xrightarrow{k_2} A + C_6H_5\dot{C}H\text{-CHCl-}C_6H_5 + Cl^- \tag{2}$$

$$A^{\cdot-} + C_6H_5\dot{C}H\text{-CHCl-}C_6H_5 \xrightarrow{k_3} A + C_6H_5\bar{C}H\text{-CHCl-}C_6H_5 \tag{3}$$

$$C_6H_5\text{-}\bar{C}H\text{-CHCl-}C_6H_5 \xrightarrow{k_4} C_6H_5CH=CHC_6H_5 + Cl^- \tag{4}$$

Scheme 1.

lic voltammetry (CV) and double potential step chronoamperometry (DPSC). The electron transfer from the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (1^-) was included in the investigation.

Preparative reductions. The indirect reduction of d,l-1,2-dibromo-1,2-diphenylethane using chloranil as mediator and of 2-dl using quinoxaline as electron transferring agent have been reported previously; *trans*-stilbene was the only product isolated.[4]

The *vic*-dihalides 2-m and 2-dl were chosen as electron acceptors since the reaction route was believed to be reasonably well understood and relatively simple, whereas the indirect reduction of alkyl halides[5,6] and benzyl chlorides[7] has been shown to follow reaction paths complicated by either coupling or follow-up reactions due to the formation of strong bases or nucleophiles.

The anion 1^- has been shown to couple with both aliphatic[6,8] and benzylic[7] halides in high yield; however, the reaction of 1^- with 2-dl turned out to be a purely catalytic reduction of 2-dl to *trans*-stilbene with no coupled products. The reduction of 2-dl by an anion radical is assumed to follow Scheme 1, and the kinetic data are calculated assuming this scheme.[4] When 1^- is used as a mediator, A and $A^{\cdot-}$ in Scheme 1 should be exchanged with $1^{\cdot}$ and 1^-, respectively, where $1^{\cdot}$ is the radical obtained by oxidation of 1^-.

In Scheme 1, k_3 and k_4 are assumed to be large compared to k_2 ($= k_{ET}$); it has previously been inferred[4] that k_4 is comparable in magnitude to the rate constant for rotation about the central carbon-carbon bond, and the proposal that k_3 is greater than k_2 is plausible, since the radical is more easily reduced than 2-dl.

Table 1. Rate constants for electron transfer from some electron donors to *meso*-1,2-dichloro-1,2-diphenylethane (2-m). The rate constants (in $M^{-1} s^{-1}$) were determined by cyclic voltammetry (k_{CV}) and double potential step chronoamperometry (k_{DPSC}); their mean value is k_M. Uncertainties in the determination of k_M are 10–20 %.Solvent: DMF/TBABF$_4$.

Donor	$-E_A°/V$	k_{CV}	k_{DPSC}	k_M	log k_M	$\Delta G^{\ddagger}$/kcal mol^{-1}
Azobenzene	0.879	7.9	10.6	9.3	0.97	13.68
p-Diacetylbenzene	1.006	212	273	243	2.39	11.74
Quinoxaline	1.200	7390	7470	7430	3.87	9.72
Perylene	1.213	13950	13960	13955	4.14	9.36
Benzophenone	1.32	13250	14940	14100	4.15	9.34
9,10-Diphenyl-anthracene	1.404	240000	–	240000	5.38	7.67
3	1.32	13200	14600	13900	4.14	9.36
4	1.34	40200		40200	4.60	8.73
1^-	1.13	934	962	948	2.98	10.94

Table 2. Rate constants in DMF/TBABF$_4$ for electron transfer from some electron donors to *d,l*-1,2-dichloro-1,2-diphenylethane (2-*dl*). The rate constants (in M^{-1} s^{-1}) were determined by CV (k_{CV}) and DPSC (k_{DPSC}); their mean value is k_M.

| Donor	$-E_A°$/V	k_{CV}	k_{DPSC}	k_M	log k_M	$\Delta G^{\ddagger}$/kcal mol^{-1}
p-Diacetylbenzene	1.006	65	–	65	1.81	12.54
Quinoxaline	1.200	1954	2696	2325	3.36	10.42
Perylene	1.213	4924	4919	4922	3.69	9.97
Benzophenone	1.32	7065	6779	6922	3.84	9.77
9,10-Diphenyl-anthracene	1.404	90000	89700	90000	4.95	8.25
Anthracene	1.488	202700	184300	193500	5.29	7.22
3	1.32	4200	4040	4120	3.61	10.08
4	1.34	13700	11700	12700	4.10	9.41
1$^-$	1.13	376	–	376	2.57	11.50
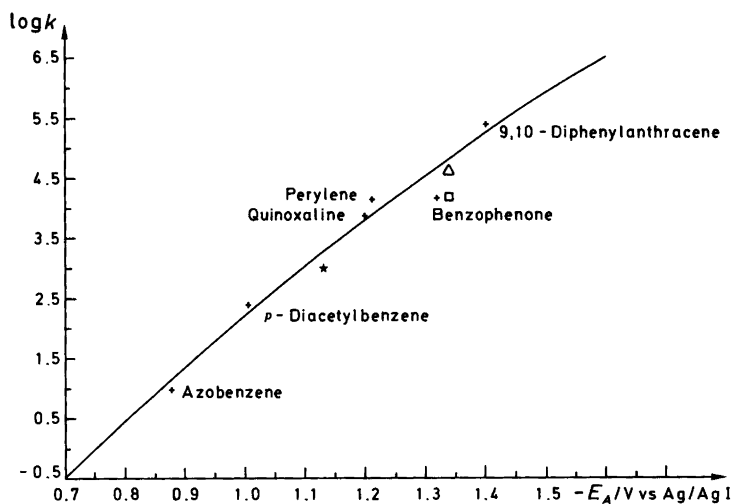
Fig. 1. Dependence of rate constants for the reaction between different electron donors and *meso*-1,2-dichloro-1,2-diphenylethane on the reversible redox potential of the donors; ★ **1**$^-$, □ **3**, △ **4**.
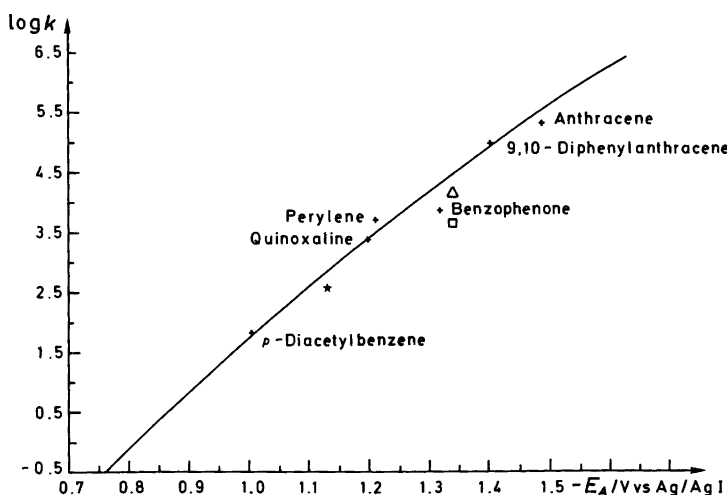

Fig. 2. Dependence of rate constants for the reaction between different electron donors and *d,l*-1,2-dichloro-1,2-diphenylethane on the reversible redox potential of the donors; ★ **1**$^-$, □ **3**, △ **4**.

Electroanalytical experiments. The principle aim of this investigation was to establish curves depicting the dependence of the rate constants for electron transfer from a number of anion radicals to a given halide on the reversible redox potential of the anion radicals. A comparison of the observed rate constants for electron transfer from the electron donors 1^-, **3** and **4** with the curve would establish whether any special effects were operating. The rate constants were determined using cyclic voltammetry (CV) and double potential step chronoamperometry (DPSC).[9]

The kinetic data for the catalytic reduction of **2-***dl* and **2-***m* are given in Tables 1 and 2 and depicted in Figs. 1 and 2. The rate constants were obtained by comparing experimental data with simulated values calculated assuming Scheme 1 to be correct. It can be seen (Tables 1 and 2) that the correspondence between the data obtained by CV and those obtained by DPSC is acceptable to good. To illustrate the procedure and the uncertainties in the determination of the rate constants, the measured data used for the calculation of a single k_{CV} and a single k_{DPSC} rate constant are presented in Table 4. Typically, the standard deviation for a series of CV and DPSC measurements obtained for the same solution is 4–10 %. The reproducibility between a series of measurements obtained for two different solutions is in the range of 10–20 %.

By comparing data for **2-***dl* and **2-***m* it is found that the rate of electron transfer to **2-***m* is 3–4 times faster than to **2-***dl*; this may reflect differences in preferred conformation.

In Table 3, the observed rate constants for 1^-, **3** and **4** are compared with the values predicted from Figs. 1 and 2; the measured rate constants for 1^-, **3** and **4** are close to the predicted values.

The measured rate constant (k_M) for **4** is a factor of 3($\pm$0.8) higher than that for **3**. A small part of this enhancement can be attributed to the slightly more negative redox potential of **4** relative to that of **3**. The remaining enhancement,

$$[k_M(4)/k_{exp}(4)]/[k_M(3)/k_{exp}(3)] \sim 2.4,$$

although measurable, is small and it is not possible to draw any conclusions concerning the nature and origin of this effect.

The reductive elimination of halide from *vic*-halides by anions such as iodide has usually been depicted as an S_N2-like attack of iodide on the halogen, with atom transfer (Scheme 2). It is observed that *trans*-stilbene formation by the reductive elimination of **2-***dl* and **2-***m* in the presence of 1^- proceeds at a rate close to that predicted from Figs. 1 and 2. This strongly suggests that the rate-determining step is the outer-sphere transfer of an electron.

The data obtained for this purely catalytic reduction with 1^- as donor also have a bearing on the reorganization energy (λ) associated with the electron transfer from 1^-. It has previously been argued[6] that λ for 1^- should be close to a typical λ for aromatic hydrocarbons ($\sim$10 kcal mol^{-1}),

$$R\text{-}CH\text{-}CH\text{-}R' \longrightarrow R\text{-}CH=CH\text{-}R' + IX + X^- \quad (5)$$

$$I^- + IX \rightarrow I_2 + X^- \quad (6)$$
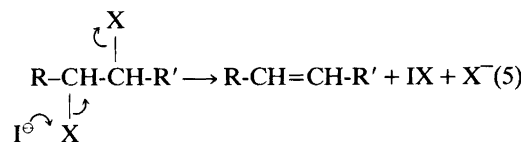
Scheme 2.

Table 3. Comparison of the experimental rate constants (k_M) for the reactions between 1^-, **3** or **4** and **2-***m* and **2-***dl*, and the rate constants expected (k_{Exp}) for an uncomplicated outer-sphere electron transfer, obtained from Figs. 1 and 2.

Donor	Acceptor	k_M/M^{-1} s^{-1}	k_{Exp}/M^{-1} s^{-1}	k_M/k_{Exp}	$k_M(4)/k_M(3)$
1^-	**2-***dl*	376	693	0.55	–
3	**2-***dl*	4120	21300	0.19	–
4	**2-***dl*	12700	27900	0.46	3.1
1^-	**2-***m*	948	1745	0.54	–
3	**2-***m*	13900	46000	0.30	–
4	**2-***m*	40200	63095	0.64	3

since $\mathbf{1}^-$ has extended π-electron conjugation. The reactions between anion radicals and **2** and between $\mathbf{1}^-$ and **2** are purely catalytic reductions; the rate of the reaction between $\mathbf{1}^-$ and **2** (Table 3) falls on the E° vs. log k curve for anion radicals (Figs. 1 and 2), which strongly suggests that the activation energy for electron transfer (and thus the reorganization energy λ) should be nearly the same for $\mathbf{1}^-$ and for aromatic anion radicals, and thus that λ for the self-exchange reaction

$$\mathbf{1}^\bullet + \mathbf{1}^- \rightleftarrows \mathbf{1}^- + \mathbf{1}^\bullet$$
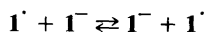
should be about 10 kcal mol^{-1}.

A comparison of the reactions between the substrates t-butyl bromide,[6] benzyl chloride[7] and 1,2-dichloro-1,2-diphenylethane, and the electron donors $\mathbf{1}^-$ and the aromatic anion radicals $A^{\bullet-}$ shows that $\mathbf{1}^-$ and $A^{\bullet-}$ react with t-butyl bromide almost exclusively with coupling, benzyl chloride reacts with $\mathbf{1}^-$ with coupling and with $A^{\bullet-}$ with electron transfer, whereas **2** reacts with both $\mathbf{1}^-$ and $A^{\bullet-}$ with electron transfer without coupling. The redox potential of the radicals is probably an important factor in deciding which type of reaction is favoured.

Experimental

Materials. Solvents and electrolytes were purified as described in earlier papers from this laboratory. The preparation and characterisation of compounds **2-dl** and **2-m** have also been described previously.[4]

Electrochemical apparatus. Conventional glass cells with sintered-glass separators were used. The apparatus for CV and DPSC experiments was that used previously.[6]

Controlled potential electrolyses. Reduction of 2-dl *by* $\mathbf{1}^-$. 4-Methoxycarbonyl-1-methylpyridinium iodide ($\mathbf{1}^+$; 254 mg, 1.03 mmol) was reduced in DMF in the presence of **2-dl** (450 mg, 1.79 mmol) at an Hg cathode [-1.20 V vs. Ag/ AgI, Bu$_4$NBF$_4$]. Reduction was complete after the consumption of 411 C (2.38 F mol^{-1} w.r.t. **2-dl**). A known weight of naphthalene was added to the catholyte, which was analysed by GLC [25 % cyanopropyl column (15 m); temperature programme 50 °C/4 min, then to 200 °C at 5 °C min^{-1}; nitrogen flow rate 2 ml min^{-1}]. The yield of *trans*-stilbene, measured against the naphthalene internal standard, was quantitative.

Reduction of 2-m *by* $\mathbf{1}^-$. The catalyst $\mathbf{1}^+$ (0.11 g, 0.39 mmol) and **2-m** (0.30 g, 1.2 mmol) were co-

Table 4. Measured CV and DPSC data used in the calculation of the rate constant k for electron transfer from perylene anion radical to d,l-1,2-dichloro-1,2-diphenylethane (2-dl). The CV and DPSC measurements were performed on the same solution. C_A and C_{BX} are the concentrations of perylene and 2-dl, respectively, v the scan rate, $I_{p,a}$ and $I_{p,c}$ the anodic and cathodic peak currents, τ the pulse time and $i(\tau)$, (2τ) the currents measured at time τ and 2τ, respectively.

C_A/ mM	C_{BX}/C_A	v/ V s^{-1}	$I_{p,a}/I_{p,c}$	k_{CV}/ $10^3 \times$ M^{-1} s^{-1}	τ/ ms	$i(2\tau)/i(\tau)$	k_{DPSC}/ $10^3 \times$ M^{-1} s^{-1}
1.98	1.0	1.00	0.13	6.00	19.0	0.179	4.93
1.98	1.0	1.50	0.19	5.08	19.0	0.179	4.93
1.98	1.0	1.71	0.22	4.80	16.9	0.143	5.13
1.98	1.0	2.01	0.25	4.72	15.0	0.155	4.94
1.98	1.0	2.50	0.27	4.98	10.3	0.179	5.50
1.98	1.0	3.00	0.31	4.86	8.1	0.199	4.14
1.96	2.0	2.50	0.12	4.73	11.2	0.123	4.62
1.96	2.0	3.00	0.15	4.76	10.3	0.129	4.75
1.96	2.0	4.01	0.21	4.60	9.2	0.132	5.10
1.96	2.0	5.00	0.25	4.39	8.1	0.143	5.18
1.96	2.0	6.01	0.28	4.89	–	–	–

$<k_{CV}> = (4.93 \pm 0.19) \times 10^3$ M^{-1} s^{-1} $\qquad$ $<k_{DPSC}> = (4.92 \pm 0.16) \times 10^3$ M^{-1} s^{-1}

electrolysed as described above, at -1.10 V. The cell current from 6 mA cm^{-2} to a 1 mA cm^{-2} after the passage of 1.6 F mol^{-1}. The product, *trans*-stilbene, was extracted into ether after dilution of the electrolyte with water; yield 0.18 g, 84 %.

Reduction of 2-m *by* 3$^-$. Similar co-electrolysis of 2-*m* (0.30 g, 1.2 mmol) and 3 (0.05 g, 0.4 mmol) gave, after the passage of 2.0 F mol^{-1}, *trans*-stilbene (0.17 g, 80 %).

Kinetic measurements. The rate constants were determined using CV and DPSC.[6,9] Measured rate data for the electron transfer from perylene anion radical to 2-*dl* are shown in Table 4. Medium: DMF/O.1M TBABF$_4$.

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