Hz), 6.74 and 6.80 (s, s, arom H's).

Optically active cryptophane G ((+)-**3**) was similarly prepared from 100 mg of (−)-**11c** in 2 mL of $CHCl_3$ and 200 mL of formic acid for 1 h at 90 °C. TLC separation as above gave 35 mg of (+)-**3**, $[\alpha]_D$ +199° ($CHCl_3$, *c* 0.43), and 22 mg of **8** (showing no rotation). (+)-**3** was recrystallized from methanol: yield 28 mg, 30%; $[\alpha]_D$ +201° ($CHCl_3$, *c* 0.44; see Tables I and II). **8** was recrystallized from acetone; yield 13 mg, 14%. ^1H NMR spectra of (+)-**3** and **8** were identical with those of *rac*-**3** and *meso*-**8** given above.

Cryptophanol A (*rac*- and (−)-4). ***rac*-4**: To 225 mg (0.25 mmol) of *rac*-**1** was added 3 mL of a 1 M THF solution of lithium diphenylphosphide,[21b] and the resulting deep red mixture was stirred at room temperature for 24 h under argon atmosphere. Water was added, and some neutral material was extracted with ether. On acidification (concentrated HCl), the aqueous phase afforded a white precipitate of **4**, which was collected by suction filtration, washed with water, and then digested in refluxing THF: yield 125 mg (60%); mp >260 °C; C, H analysis, consistent with a *trihydrate*; ^1H NMR (from Me_4Si in CD_3COCD_3) δ 3.16 (d, H_e) and 4.40 (d, H_a, J = 13.5 Hz), 4.40 (s, OCH_2), 6.63 and 6.73 (s, s, arom H), 7.7 (OH). Anal. Calcd for $C_{48}H_{42}O_{12}{\cdot}3H_2O$: C, 66.66; H, 5.59. Found: C, 67.0; H, 5.3.

(−)-**4**: The (−) enantiomer of **4** was similarly prepared from 50 mg of (−)-**1** (0.056 mmol) having $[\alpha]_D$ −231° ($CHCl_3$) and 1.5 mL of 1 M lithium diphenylphosphide in THF. For the CD measurements, a sample was recrystallized from THF: $[\alpha]_D$ −172° (DMF, *c* 0.21; see Tables I and II); analytical TLC behavior of (−)-**4**, identical with that of the racemate (dichloromethane/methanol, 95:5 (v/v)).

Cryptophanol A Hexaacetate ((−)-5). This compound was prepared by reaction of (−)-**4** (12 mg) and acetic anhydride (0.5 mL) in 1 mL of pyridine for 1 h at room temperature. The solution was poured into water, and the precipitate of (−)-**5** was collected by suction filtration and was finally purified by TLC (dichloromethane/acetone, 9:1 (v/v)) and by digestion in ether: yield 9 mg of a solid (mp >260 °C); $[\alpha]_D$ −24° ($CHCl_3$, *c* 0.24; see Tables I and II); ^1H NMR (from internal Me_4Si in $CDCl_3$) δ 2.35 (s, $OCOCH_3$), 3.48 (d, H_e) and 4.58 (d, H_a, J = 13.7 Hz), 3.80–4.35 (m, OCH_2CH_2O), 6.86 and 6.92 (s, s, arom H).

Cryptophanol A, Hexakis[*O*-(carbomethoxy)methyl] (*rac*- and (−)-6). To *rac*-**4** (50 mg, 0.0617 mmol) in DMF (2 mL) was added 125 mg (0.38 mmol) of Cs_2CO_3; after 1 h stirring at room temperature, 0.075 mL (ca, 2 equiv) of methyl bromoacetate was added, and the mixture was heated for 20 h at 60 °C under nitrogen. Water was added, and the precipitate was collected by suction filtration, washed with methanol, and then recrystallized from chloroform–methanol: yield 50 mg (65%); mp ca. 195 °C; FAB$^+$ mass spectrum, M$^+$ *m/z* 1243.54 (calcd 1243.27); C,H analysis, consistent with a *tetrahydrate*. ^1H NMR (from Me_4Si in CD_3COCD_3) δ 3.34 (d, H_e) and 4.55 (d, H_a, J = 13.6 Hz), 3.82 (s, $COOCH_3$), 4.41 (m, OCH_2CH_2O), 4.66 and 4.77 (AB q, OCH_2CO_2 (diastereotopic H, J = 15.9 Hz)), 6.82 and 6.89 (s, s, arom H). Anal. Calcd for $C_{66}H_{66}O_{24}{\cdot}4H_2O$: C, 60.27; H, 5.67. Found: C, 60.04; H, 5.3.

Similarly, 37 mg of (−)-**4**, 100 mg of Cs_2CO_3, and 0.075 mL of methyl bromoacetate in 1.5 mL of DMF gave 28 mg (53%) of (−)-**6**, after TLC and recrystallization from chloroform/methanol: $[\alpha]_D$ −116° ($CHCl_3$, *c* 0.39; see Tables I and II); analytical TLC and ^1H NMR, identical with that of the racemate.

Chemical vs. Redox Catalysis of Electrochemical Reactions. Reduction of *trans*-1,2-Dibromocyclohexane by Electrogenerated Aromatic Anion Radicals and Low Oxidation State Metalloporphyrins

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Received February 13, 1987

Abstract: Homogeneous catalysis of the electrochemical reduction of *trans*-1,2-dibromocyclohexane is investigated in a series of catalysts comprising aromatic and heteroaromatic compounds and several metalloporphyrins. The aromatic anion radicals and the reduced Zn and Cu porphyrins give rise to a typical redox catalysis involving an outer-sphere electron transfer from the mediator to the substrate. The rate-determining step of the reaction as well as that of the direct electrochemical reduction at glassy carbon consists of the injection of one electron concerted with the cleavage of one carbon–bromine bond. The final olefin is obtained in successive steps after injection of a second electron and cleavage of a second bromide ion. The direct reduction and the redox-catalyzed reaction follow the same quadratic activation driving force free energy relationship involving two additive reorganization factors. One, accounting for about 80% of the standard activation energy, concerns the breaking of the C–Br bond giving a contribution approximately equal to one-fourth of the bond dissociation energy. The remainder of the activation barrier involves solvent reorganization. Nickel, iron, and cobalt porphyrins (at the formal metal "I" oxidation state) react much more rapidly than redox catalysts having the same standard potential. This points to an inner-sphere mechanism: abstraction of one Br followed by or concerted with the elimination of the second Br or S_N2 displacement of one Br$^-$ followed by or concerted with the elimination of the second Br$^-$ before or after the injection of a second electron.

Very numerous electrochemical reactions require a significant overpotential to proceed at appreciable rates owing to the slowness and irreversibility of the electron transfer and/or chemical steps they involve. Homogeneous catalysis of such electrochemical processes may be carried out along two conceptually different types of mechanisms.[1] In one case, "redox catalysis",[1] the active form of the catalyst, generated at the electrode, exchanges electrons with the reactant in an outer-sphere manner yielding the reaction products and regenerating the starting form of the catalyst. Catalysis[2] then results from physical rather than chemical reasons: the possibility of diminishing the overpotential is a consequence of the three-dimensional dispersion of the electron-transfering agent as opposed to the two-dimensional availability of the

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(1) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *87*, 39.

(2) In both cases the efficiency of the catalysis is referred to an outer-sphere electrode process in which there is no surface catalysis of the reaction by the electrode material.

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electrons (or holes) at the electrode surface.

On the other hand, "chemical catalysis"[1,2] involves the transient formation of an adduct between the active form of the catalyst and the reactant. The chemical bond thus formed has to be cleaved successively or after the exchange of additional electrons for eventually yielding the products and regenerating the starting form of the catalyst.

Although the examples of homogeneous catalysis of electrochemical reactions are numerous both at the preparative ("indirect electrolysis") and the microelectrolytic scale,[3] it is not always straightforward to distinguish between the two types of catalysis and therefore to find guidelines for designing efficient catalytic systems.

How the catalytic efficiency is related to the nature of the catalyst, through its standard potential, is well understood in the case of redox catalysis.[1,4] The resulting kinetic laws have been amply illustrated experimentally with examples in the reduction of aromatic[5] and aliphatic halides[6] in aprotic solvents. For the purpose of the present discussion, it is sufficient to recall the following. When the intermediate, B, resulting from the initial electron transfer between the active form of the catalyst, Q, and the substrate, A, is very unstable, leading rapidly to another species C or when the conversion of A into C involves a concerted electron-transfer–chemical (e.g., bond breaking) process, the rate-determining step is the forward electron transfer (Scheme I, eq 1). The catalytic efficiency is then an increasing function of the corresponding rate constant k_1, which is itself related to the difference between the standard potential of the redox catalyst, E°_{PQ}, and the redox potential characterizing the substrate, E°_A, according to a Bronstedt–Marcus activation driving force free energy relationship.[7,14] It is thus quite possible to predict how the catalytic efficiency, in term of currents, decreases when the standard potential of the redox catalyst becomes less and less negative (for a reduction, and less and less positive for an oxidation).

Scheme I

$$P + e \rightleftarrows Q \qquad (0)$$

$$Q + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} P + B \qquad (1)$$

$$B \xrightarrow{k_2} C \qquad (2)$$

Identification of a chemical catalysis process is more difficult. Thus far, the only approach has been to characterize the intermediate adduct formed by reaction of the active form of the catalyst with the substrate. A typical example, which has been previously described, is the reduction of aliphatic halides by electrogenerated iron(I) and iron("0") porphyrins,[8] where the $Fe^{III}R$, $Fe^{II}R^-$, and $Fe^{I}R^{2-}$ intermediate adducts have been identified. A drawback of this method is that the identification of the intermediate adduct requires that it is not too unstable which limits the efficiency of the catalytic process. Catalytic processes well characterized along this approach would thus be poorly efficient in most cases.

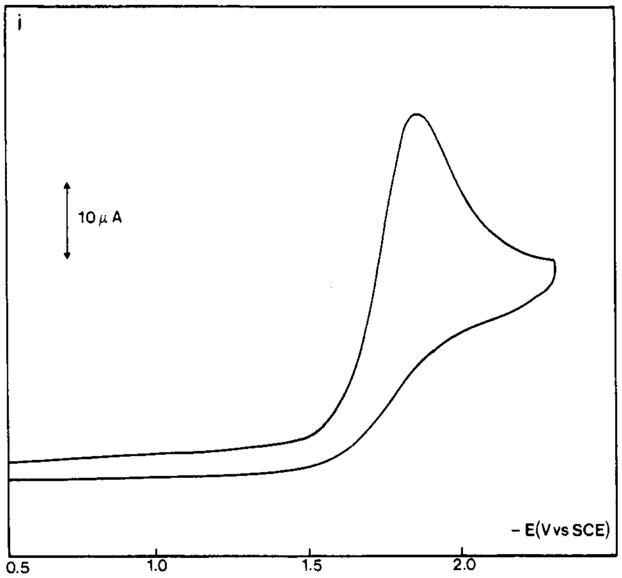
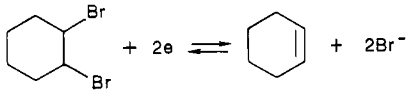


Figure 1. Cyclic voltammetry of *trans*-1,2-dibromocyclohexane (1.35 mM) in DMF (+0.1 M Et_4NClO_4) at a glassy carbon electrode: temperature, 21 °C; sweep rate, 0.1 V·s^{-1}.

In the following, we describe another approach to the problem which consists in comparing chemical and redox catalysis of the same reduction process, in terms of catalytic efficiency and thus of rate constants of the rate-determining step, as a function of the driving force offered by the catalyst couple, itself measured by its standard potential. The illustrating example we choose is the reduction of a vicinal dihalide, *trans*-1,2-dibromocyclohexane (DBC), into the corresponding olefin



according to an overall two-electron reaction involving the cleavage of the two carbon–halogen bonds.[9] Besides its direct electrochemical reduction, we investigated its reaction with electrogenerated aromatic anion radicals on one hand and reduced states

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[3] (a) Kolthoff, I. M.; Lingane, J. J.; *Polarography*; Interscience: New York, 1952; Vol. 1. (b) Heyrovsky, J.; Kuta, J. *Principles of Polarography*; Academic Press: New York, 1966. (c) Mairanovsky, V. G. *Catalytic and Kinetic Waves in Polarography*; Plenum Press: New York, 1968. (d) Simonet, J. "Electro-Generated Reagents" In *Organic Electrochemistry*, 2nd ed.; Baizer, M. M., Lund, H., Eds.; Marcel Dekker: New York, 1983; pp 843–861.

[4] (a) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *87*, 55. (b) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *Ibid.* **1978**, *78*, 43. (c) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *Ibid.* **1980**, *113*, 1. (d) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *Ibid.* **1980**, *113*. 19. (e) Savéant, J. M.; Su, K. B. *Ibid.* **1984**, *171*, 341. (f) Savéant, J. M.; Su, K. B. *Ibid.* **1985**, *196*, 1. (g) Nadjo, L.; Savéant, J. M.; Su, K. B. *Ibid.* **1985**, *196*, 23. (h) Andrieux, C. P.; Hapiot, P.; Savéant, J. M. *Ibid.* **1985**, *189*, 121. (i) Andrieux, C. P.; Savéant, J. M. *Ibid.* **1986**, *205*, 43.

[5] (a) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3431. (b) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 3806.

[6] (a) Andrieux, C. P.; Merz, A.; Savéant, J. M.; Tomahogh, R. *J. Am. Chem. Soc.* **1984**, *106*, 1937. (b) Andrieux, C. P.; Merz, A.; Savéant, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 6097. (c) Andrieux, C. P.; Gallardo, I.; Savéant, J. M.; Su, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 638. (d) Andrieux, C. P.; Savéant, J. M.; Su, K. B. *J. Phys. Chem.* **1986**, *90*, 3815.

[7] (a) E°_A is the standard potential of the A/B couple when the conversion of A into C involves B as an intermediate. It is the standard potential of the A/C couple when the conversion of A to C is a concerted electron transfer bond breaking process.[6a,14] (b) k_1 then decreases as the standard potential of the catalyst E°_{PQ} becomes more positive in a linear or slightly parabolic manner.

[8] (a) Mispelter, J.; Lexa, D.; Savéant, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 6806. (b) Lexa, D.; Savéant, J. M.; Wang, D. L. *Organometallics* **1986**, *5*, 1428.

[9] (a) The direct electrochemical reduction of vicinal dihalides in general has been shown to proceed in this manner.[9b–f] The reduction of vicinal dihalides has previously been taken as a test example of demonstrating the catalytic properties of modified electrodes in the case of poly-*p*-nitrostyrene coatings[9g,h] and of metalloporphyrin polymer coatings.[9i] (b) Hawley, M. D. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Lund, H., Eds.; Marcel Dekker: New York, 1980; Vol XIV, Organic Section. (c) Becker, J. Y. *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Chapter 6, pp 203–285. (d) Anderson, J. T.; Stocker, J. H. "Stereochemistry of Organic Electrode Processes" In *Organic Electrochemistry*; Baizer, M. M., Lund, H., Eds.; Marcel Dekker: New York, 1983; pp 932–941. (e) A thorough study of the influence of the equatorial–equatorial/axial–axial isomerism on the reduction of DBC at low temperatures has been carried out in butyronitrile on a mercury electrode.[9f] The comparison with the present results is not straightforward owing to the difference in temperature and electrode material. (f) O'Connell, K. M.; Evans, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 1473. (g) Van de Mark, M. R.; Miller, L. L. *J. Am. Chem. Soc.* **1978**, *100*, 3223. (h) Kerr, J. B.; Miller, L. L. *J. Electroanal. Chem.* **1979**, *101*, 263. (i) Rocklin, R. D.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 2104.

Table I. Catalysis of the Reduction of DBC by the OEPFe^{II}/OEPFe^{I} Couple Rate Constant (M^{-1}·s^{-1}) for Various Sweep Rates and Catalyst Concentrations

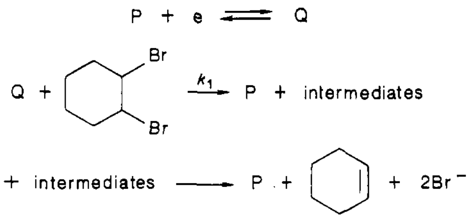
catalyst concn (mM)	sweep rate (V·s^{-1}) 0.1	0.2
0.98	0.9510^5	1.210^5
0.214	1.110^5	1.110^5

of various metalloporphyrins on the other, in the octaethylporphyrin (OEP) series, in the context of homogeneous catalysis of the electrochemical reduction of DBC.

Results

Figure 1 shows a typical cyclic voltammogram obtained for the reduction of DBC in dimethylformamide (DMF) at a glassy carbon electrode. The peak height was found to vary proportionally with the concentration and the square root of the sweep rate and to correspond to a two-electron per molecule stoichiometry. The peak width, $E_{p/2} - E_p$ (E_p and $E_{p/2}$ are the peak and half-peak potentials), was found independent of both factors and to have an average value of 133 ± 5 mV. This corresponds to a transfer coefficient, α, equal to[10] 0.352 ± 0.008. The peak potential was found equal to −1.840 ± 0.003 V vs. SCE at a sweep rate of 0.1 V·s^{-1}. It was observed to vary linearly with the logarithm of the sweep rate at a rate which fits with the above value of α^{10} within experimental uncertainty.

All the catalysts investigated (see Table III) gave rise to reversible cyclic voltammograms in the absence of DBC. Upon addition of DBC, the cathodic peak height increases, and its reversibility is gradually lost. The ratio of the peak currents obtained in the presence and absence of the catalyst, respectively, and its variations with the excess factor γ, i.e., the ratio between the concentrations of substrate and catalyst, is an experimental observable that allows the determination of the rate constant of the rate-determining step of the overall reaction.[4d] The reaction mechanism that was tested in this connection is the following



where the rate of the third step is assumed to be much faster than the second. This gives rise to the same formal kinetics as the "SET" mechanism investigated previously.[4d] We introduced two slight modifications vis-à-vis the previous treatments.[4] One concerns the possible inequality of the diffusion coefficients of the catalyst and substrate. Their ratio was derived from the peak heights of the voltammograms of the catalyst and the substrate in separate solutions. The resulting values were taken into account in the treatment of data according to an already described procedure.[4h] On the other hand, it was observed that when the catalyst standard potential comes close to the direct reduction peak potential, overlap between the two waves cannot be neglected. Also, for larger potential separations but with weak catalysts, the direct reduction influences the height of the catalytic wave. This was taken rigorously into account in the treatment described in the Experimental Section, based on an experimental observable which, rather than the ratio of peak currents in the presence and absence of the substrate, was defined as the ratio of the currents in the presence and absence of the substrate at a potential equal to the peak potential of the catalyst in the absence of the substrate.

Typical results are shown in Figure 2 for the example of OEPFe under the form of the variations of the current ratio as defined above with the ratio of the substrate and catalyst concentrations.

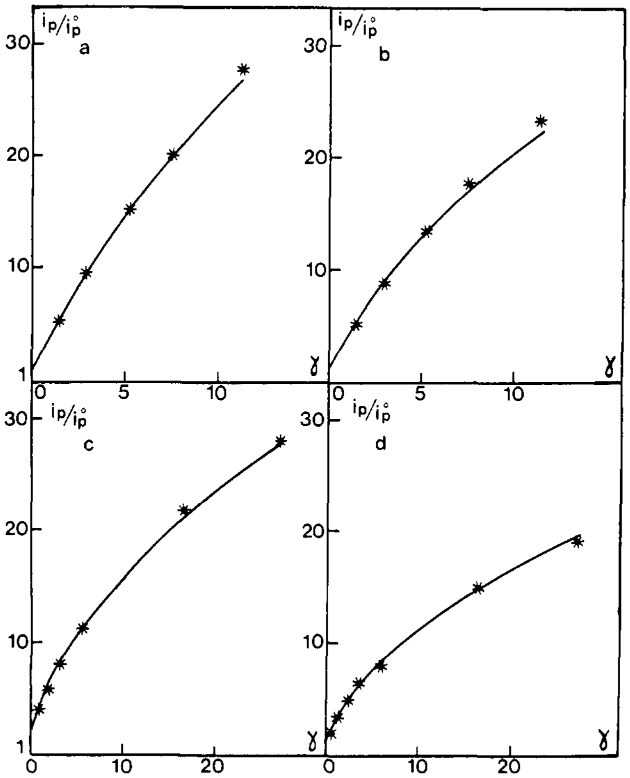


Figure 2. Homogeneous catalysis of the electrochemical reduction of *trans*-1,2-dibromocyclohexane by the iron(II)/iron(I) couple of OEPFe. Peak current ratio i_p/i°_p (i_p and i°_p are the currents, in the presence and absence of DBC, respectively, at a potential equal to the peak potential of the catalyst in the absence of the substrate) as a function of the ratio of the substrate and catalyst concentrations, γ: catalyst concentration, 0.98 mM (a, b), 0.214 mM (c, d); sweep rate, 0.1 V·s^{-1} (a, c), 0.2 V·s^{-1} (b, d); temperature, 21 °C; solvent, DMF + 0.1 M Et_4NClO_4.

Table II. Homogeneous Catalysis of the Reduction of DBC by Aromatic Anion Radicals and Reduced Metalloporphyrins; Rate Constant of the Rate-Determining Step[a]

catalyst[d]	E°_{PQ} (V vs. SCE)[b]	d[c]	k (M^{-1}·s^{-1})
perylene	-1.62_0	1.43	$5.0\ 10^4$
OEPZn	-1.56_0	2.60	$1.9\ 10^4$
terephthalonitrile	-1.50_0	1.42	$5.7\ 10^3$
benzo[*c*]chinoline	-1.45_0	1.43	$6.2\ 10^2$
OEPCu	-1.42_5	2.60	$2.9\ 10^3$
OEPNi	-1.35_0	2.60	$5.9\ 10^4$
$OEPH_2$	-1.29_3	2.60	$1.0_5\ 10^2$
fluorenone	-1.23_0	1.15	$1.0\ 10^1$
OEPFe	-1.20_3	2.60	$1.1\ 10^5$
OEPCo	-0.97_0	2.60	$1.6\ 10^5$

[a] At 21 °C, in DMF + 0.1 M Et_4NClO_4. [b] Standard potential of the catalyst couple. [c] Ratio of the catalyst over DBC diffusion coefficients. [d] OEP designates the nonmetallated octaethylporphin ("free base") and OEPZn, Cu, Ni, Fe, Co, the corresponding metalloporphyrins.

Table III. Preparative Scale Direct and Mediated Reduction of *trans*-1,2-Dibromocyclohexane[a]

catalyst	redn potntl[b]	concentrations (mM) catalyst	DBC	no. of electron[c]	cyclohexene yields[d] (%)
terephthalonitrile	−1.50	5.0	14.6	1.94	86.3
OEPNi	−1.60	0.325	13.14	2.13	99.7
OEPFe	−1.60	0.68	14.6	1.87	98.6

[a] In DMF + 0.1 M Et_4NClO_4, at a carbon electrode; temp, 21 °C. [b] In V vs. SCE. [c] Per molecule of DBC consumed. [d] Number of moles of cyclohexene formed per mole of DBC consumed. [e] Direct reduction.

Fitting of the experimental data with the theoretical working curves leads to the following values of the rate constant of the rate-determining step (Table I). There is an excellent agreement

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(10) (a) Matsuda, H.; Ayabe, Y. *Z. Elektrochem.* **1955**, *59*, 494. (b) Nadjo, L.; Savéant, J. M. *J. Electroanal. Chem.* **1973**, *44*, 327.

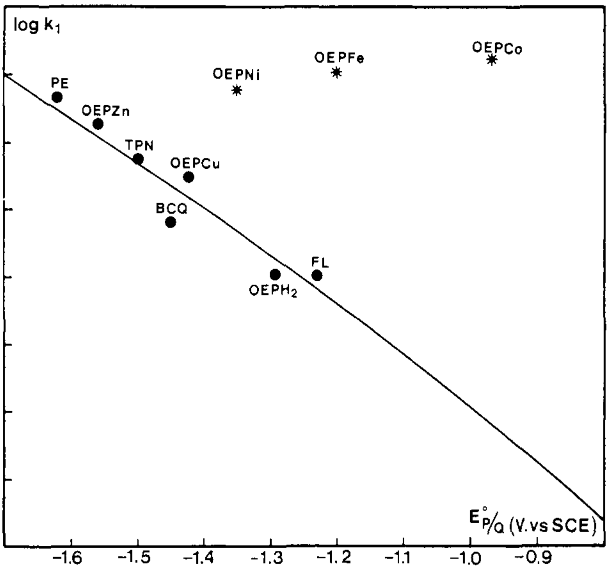

Figure 3. Homogeneous catalysis of the electrochemical reduction of *trans*-1,2-dibromocyclohexane by aromatic anion radicals and reduced metalloporphyrins. Variation of the rate constant of the rate-determining step with the standard potential E°_{PQ} of the rate-determining step: (●), redox catalysts; (*), chemical catalysts; PE, perylene; TPN, terephthalonitrile; BCQ, benzo[*c*]chinolin; FL, fluorenone; OEP, octaethylporphin.

between the rate constant values confirming the validity of the assumed mechanism. The same was found with the other catalysts in the aromatic anion radical series as well as in the metalloporphyrins series. The values of the rate constant thus found are summarized in Table II. The variations of the rate constant with the standard potential of the catalyst couple are shown in Figure 3.

It immediately appears that the cobalt, iron, and nickel porphyrins are much more efficient catalysts than the aromatic anion radicals having the same standard potential. In order to check that the overall reaction remains the same in all cases we carried out preparative scale experiments for the direct electrochemical reduction and for the reduction mediated by an aromatic anion radical, that of terephthalonitrile, and by the reduced Ni(II) and Fe(II) porphyrins. In all cases, cyclohexene is the only reaction product and is formed in a practically quantitative yield.[11] The electron stoichiometry is of two electrons per molecule confirming what was found in cyclic voltammetry.

Discussion

A first striking observation is that (Figure 3) the catalysts fall in two clearly different categories: all the aromatic anion radicals (including the OEP free base) plus the Zn and Cu porphyrins, on one hand, and the Ni, Fe, and Co porphyrins, on the other. In the first series, the rate constant decreases when going to less and less negative potential according to a Bronstedt–Marcus type law, whereas the rate constant in the second series is much larger than with the catalyst of the first series that would have the same standard potential.

Let us first analyze in a more detailed manner what happens in the first series in terms of outer-sphere electron transfer[22] and attempt to correlate these homogeneous rate data with those pertaining to the direct electrochemical process.

The standard potential corresponding to the overall reaction can be estimated from thermochemical data as[12]

$$E^\circ(\mathrm{Br{>}C{-}C{<}Br/{>}C{=}C{<} + 2Br^-}) = 0.120 \text{ V vs. SCE}$$

The electrochemical reduction thus proceeds with a considerable overpotential. We note that the electrochemical transfer coefficient has a value much below 0.5. This points, as discussed previously in the case of aliphatic monohalides,[6] to the concept that electron transfer and breaking of the carbon–bromine bonds are concerted rather than stepwise processes. The small value of α then results from the fact that the standard potential of the rate-determining reaction is much positive to the observed reduction potential. Three different electron transfer-bond breaking concerted processes can be envisaged as rate-determining step of the overall $2e^- - 2Br^-$ reaction[13]

$$\mathrm{Br{>}C{-}C{<}Br + e^- \rightarrow \cdot{>}C{-}C{<}Br} \quad (1)$$

$$\mathrm{Br{>}C{-}C{<}Br + e^- \rightarrow \cdot{>}C{-}C{<}^+} \quad (2)$$

$$\mathrm{Br{>}C{-}C{<}Br + 2e^- \rightarrow {>}C{=}C{<} + 2Br^-} \quad (3)$$

In the context of a quadratic activation driving force free energy relationship[14]

$$\Delta G^\ddagger_{\mathrm{el}} = \Delta G^\ddagger_{0,\mathrm{el}} \left(1 + n \frac{E - E^\circ - \phi_r}{4\Delta G^\ddagger_{0,\mathrm{el}}} \right)^2$$

($\Delta G^\ddagger_{\mathrm{el}}$ is the activation free energy for the forward process, $\Delta G^\ddagger_{0,\mathrm{el}}$ the activation free energy at zero driving force, E the electrode potential, E° the standard potential corresponding to the rate-determining reaction, ϕ_r the potential difference between the reaction site and the solution, usually considered as located in the outer Helmoltz plane,[15] and n the number of electrons per molecule exchanged in the rate-determining step) which corresponds to a potential dependent transfer coefficient

$$\alpha = \frac{1}{2}\left(1 + n \frac{E - E^\circ - \phi_r}{4\Delta G^\ddagger_{0,\mathrm{el}}} \right)$$

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[11] With OEPCo which is difficult to solubilize in DMF (maximal concentration: 0.15 mM), the electrolysis is perturbed by the formation of an insoluble product on the electrode surface which inhibits the reduction. Whereas 90% reduction was obtained in about 40 min with the other mediators, reduction of 3.7 mM of a starting 5.6 mM DBC solution was attained after 6 h. Again, however, an excellent yield (88%) in cyclohexene was obtained.

[12] (a) The enthalpies and entropies of formation of DBC and cyclohexene are respectively as follows:[12b] $\Delta H^\circ_f = -2 \times 3.4 - 4 \times 4.95 = -26.6$ Kcal·mol^{-1}; $\Delta S^\circ_f = (2 \times 20 + 4 \times 9.42 + 18.8) - (6 \times 1.37 + 5 \times 31.2 + 36.38) = -104.12$ esu and thus, at 21 °C: $\Delta G^\circ_f = 4.03$ Kcal·mol^{-1} = 0.294 eV; $\Delta H^\circ_f = -2 \times 4.95 - 2 \times 4.76 + 2 \times 8.59 + 1.4 = -0.84$ Kcal·mol^{-1}; $\Delta S^\circ_f = (2 \times 9.42 + 2 \times 9.80 + 2 \times 7.97 + 21.5) - (6 \times 1.37 + 5 \times 31.2) = -98.07$ esu and thus, at 21 °C: $\Delta G^\circ_f = 27.91$ Kcal·mol^{-1} = 1.210 eV. In DMF, at 21 °C the standard potential vs. the SCE is obtained as[5]

$$E^\circ(\mathrm{Br{>}C{-}C{<}Br/{>}C{=}C{<} + 2Br^-}) = \frac{\Delta G_f(\mathrm{Br{>}C{-}C{<}Br}) - \Delta G^\circ_f(\mathrm{{>}C{=}C{<}})}{2} - \Delta G^\circ_f(\mathrm{Br^-}) - 0.183$$

It follows, assuming that the free energies of solvation of DBC and cyclohexene in DMF are not very different, that $E^\circ(\mathrm{Br{>}C{-}C{<}Br/{>}C{=}C{<} + 2Br^-})$ = 0.120 V vs. SCE. (b) Benson, S. W. *Thermodynamical Kinetics*, 2nd ed.; Wiley: New York, 1976.

[13] (a) The possibility that reaction 2 be a one-step reaction involving the elimination of two Br^- ions concertedly with the transfer of one electron leading directly to the cation radical was suggested to us by Prof. H. Schäfer (Münster, GFR) on the basis of the variations of the polarographic half-wave potentials of vicinal dihalides with the number of methyl groups borne by the functional carbons[13b] and a linear correlation with the ionization potentials of the alkenes. (b) Schäfer, H., private communication, Santa Barbara, CA, January 1986.

[14] (a) This can be assumed on the basis of a Marcus model[14b] of the reaction as done before in the case of alkyl monohalides.[6] In fact, Marcus theory is not adapted to the present situation, since, dealing with an outer-sphere reaction not involving the cleavage of a bond, it only takes into account the fluctual reorganization of the solvent and the changes in the vibrational characteristics of the reacting species upon electron transfer. However, as shown recently,[14c] the same quadratic expression also applies if, besides solvent reorganization, the cleavage of a bond is taken into account. The standard free energy of activation, $\Delta G^\ddagger_0$ is then the sum of two contributions involving the changes in nuclear configuration occurring upon electron transfer, bond cleavage, and solvent reorganization ($\Delta G_0^{\ddagger,\mathrm{solv}}$)

$$\Delta G^\ddagger_0 = \frac{D}{4} + \Delta G_0^{\ddagger,\mathrm{solv}}$$

The first of these terms has been shown to be approximately equal to one fourth of the bond dissociation energy.[14c] (b) Marcus, R. A. *J. Phys. Chem.* **1965**, *43*, 679. (c) Savéant, J. M. *J. Am. Chem. Soc.*, in press.

[15] Delahay, P. *Double Layer and Electrode Kinetics*; Interscience: New York, 1965.

The standard potential $E°$ and the standard activation free energy can be approximately derived from the cyclic voltammetry data as follows. At a given sweep rate, the transfer coefficient can be assumed as practically constant within a potential range comprised between the half-peak and the peak potential ($E_{p/2}$ and E_p) and to have the value α_m it has in the middle of them, E_m. It thus follows (see the Experimental Section for more details on the derivation of the relationships below) that

$$\Delta G^{\ddagger}_{0,\mathrm{el}} = \frac{1}{4\alpha_m^2}\frac{RT}{F}\ln\left(\frac{Z^{\mathrm{el}}}{k}\right) \quad \text{and}$$

$$E° = E_m + \frac{4\Delta G^{\ddagger}_{0,\mathrm{el}}\,(1 - 2\alpha_m)}{n} - \phi_r$$

with

$$\alpha_m = \frac{RT}{F}\frac{1.85}{E_{p/2} - E_p} \quad \text{and}$$

$$\frac{RT}{F}\ln\frac{Z^{\mathrm{el}}}{k} = \frac{RT}{F}\ln\left[\frac{Z^{\mathrm{el}}}{(\alpha_m n v D F/RT)^{1/2}}\right] + 0.145\frac{RT}{F}$$

(k, rate constant at E_m;Z^{el}, electrochemical collision frequency; v, sweep rate; D, diffusion coefficient). In the present case, due to the presence of two carbon–bromide bonds in the molecule, k is twice the value obtained from the above expressions. This amounts to take for Z^{el} twice its actual value. Thus taking $Z^{\mathrm{el}} = 4.05 \times 10^3$ cm·s^{-1},[16a] $D = 9{\cdot}10^{-6}$ cm^2·s^{-1}, and assuming that the double layer effect is approximately the same as with a mercury electrode, i.e., $\phi_r = -0.120$ V,[16c] it is found in the case of reactions 1 or 2 that

$$\Delta G^{\ddagger}_{0,\mathrm{el}} = 0.722 \pm 0.05 \text{ eV} \quad \text{and}$$

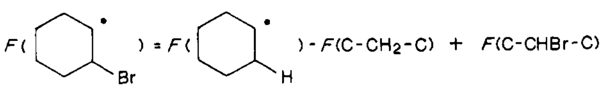
$$E° = -0.799 \pm 0.130 \text{ V vs. SCE}$$

(for the estimation of the ranges of uncertainty, see Experimental Section).

In the case of both reactions 1 and 2, there is a second electron-transfer step, the standard potential of which is the symmetric of the above $E°$ around the standard potential of the overall reaction Br>C—C<Br + 2e$^-$ ⇄ >C=C< + 2Br$^-$. Thus, the standard potential corresponding either to the reduction of the ·>C—C<Br radical into >C=C< and Br$^-$ or the reduction of the ·>C—C<$^+$ cation radical into >C=C< is thus located at 1.039 ± 0.130 V vs. SCE. This value is obviously not positive enough for corresponding to the reversible oxidation of cyclohexene into its cation radical.[17]

If we apply the same treatment of the electrochemical data as above to the case of the two-electron reaction 3, we find a standard potential of 2.050 V vs. SCE, instead of the value of 0.120 estimated from thermodynamical data (and a $\Delta G^{\ddagger}_{0,\mathrm{el}}$ of 2.86 eV), showing without ambiguity that reaction 3 does not occur as the rate-determining step in the direct electrochemical reduction.

We are thus led to conclude that the rate-determining step of the electrochemical reduction is reaction 1, i.e., the concerted transfer of one electron and the breaking of one carbon–bromine bond similarly to what has been shown to happen with alkyl monohalides.[6] The standard potential corresponding to reaction 1 can be estimated from the thermochemical data, assuming the validity of the following additivity rule for the thermodynamic formation quantities, F, of the ·>C—C<Br radical



In this way, an $E° = -0.875$ V vs. SCE is found[18] to be compared to the experimental value of −0.799. It is not surprising that the value estimated from the thermochemical data is more negative than the experimental value since the above additivity assumption neglects the stabilization of the radical by the bromine atom borne by the α-carbon.[19]

It is now possible to analyze the homogeneous kinetic data in terms of the quadratic law[20a]

$$\Delta G^{\ddagger}_{\mathrm{hom}} = \Delta G^{\ddagger}_{0,\mathrm{hom}}\left(1 + \frac{E°_{PQ} - E°}{4\Delta G^{\ddagger}_{0,\mathrm{hom}}}\right)^2$$

by using the standard potential derived from the electrochemical experimental data. Figure 3 shows the result of fitting the experimental values of the rate constant for all the homogeneous mediators but OEPNi, OEPFe, and OEPCo with the resulting parabola[20b]

$$\frac{RT}{F}\ln k_1 = \frac{RT}{F}\ln Z^{\mathrm{sol}} - \Delta G^{\ddagger}_{\mathrm{hom}}$$

It was thus found that

$$\Delta G^{\ddagger}_{0,\mathrm{hom}} = 0.792 \pm 0.09 \text{ eV}$$

The standard activation free energies of the heterogeneous and homogeneous processes can be split into two parts representing the reorganization due to bond breaking and to solvent reorientation respectively[14]

$$\Delta G^{\ddagger}_{0,\mathrm{el}} = \frac{D}{4} + \Delta G^{\ddagger,\mathrm{solv}}_{0,\mathrm{el}}$$

$$\Delta G^{\ddagger}_{0,\mathrm{hom}} = \frac{D}{4} + \Delta G^{\ddagger,\mathrm{solv}}_{0,\mathrm{hom}}$$

The last term can be evaluated on the basis of previous electrochemical and homogeneous data obtained with aromatic and heteroaromatic anion radicals in DMF in which electron transfer involves only solvent reorganization.[21] Thus taking 4Å as the radius of the sphere equivalent to the DBC molecule $\Delta G^{\ddagger,\mathrm{solv}}_{0,\mathrm{el}}$ and $\Delta G^{\ddagger,\mathrm{solv}}_{0,\mathrm{hom}}$ are found to be 0.125 and 0.132 eV, respectively. It follows that the contribution of bond breaking, as one-fourth of the bond dissociation energy D, is predicted to be comprised between 0.560 and 0.660 eV in the electrochemical case and between 0.570 and 0.750 eV in the homogeneous case. There is thus a good consistency between the heterogeneous and homogeneous data in the framework of the considered quadratic model.

On the other hand, the model will fit with an energy of one carbon–bromine bond comprised between 2.32 and 2.88 eV. The bond energy of the C–Br in DBC cannot be derived with certainty from thermochemical data for the same reasons as already discussed when evaluating the standard potential of the Br>C—C<Br + e$^-$ → ·>C—C<Br + Br$^-$ reaction. Assuming the validity of the same additivity rule one would predict an energy of 2.97 eV, i.e., very close to that of secondary monobromides. The presence of a bromine atom at the α-carbon is, as discussed earlier, likely to stabilize the ·>C—C<Br radical as compared to the ·>C—C<H radical[19] which falls in line with our results.

We can thus conclude that the kinetics of the direct electrochemical reduction and of the homogeneous reduction by aromatic radical both fit in with a quadratic model involving in the standard

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(16) (a) From the Debye–Smoluchowski equation.[16b] (b) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265. (c) Fawcett, W. R.; Ikeda, B. M.; Sellan, J. B. *Can. J. Chem.* **1979**, *57*, 2268.

(17) (a) The half-wave potential for the irreversible oxidation of cyclohexene in acetonitrile is 2.37 V vs. SCE.[17b] The standard potential of DMF of a much more conjugated hydrocarbon, anthracene, is 1.27 V vs. SCE.[17c] (b) Fleischmann, M.; Pletcher, D. *Tetrahedron Lett.* **1968**, 6255. (c) Freed, D. J.; Faulkner, L. R. *J. Am. Chem. Soc.* **1971**, *93*, 2097.

(18) For ·>C—C<Br:[12] $\Delta H°_f = 13 - (-4.95) + (-3.4) = 14.55$ Kcal·mol^{-1}; $\Delta S°_f = (76 - 9.42 + 37.8) - (6 \times 1.37 + 5 \times 31.2 + 0.5 \times 36.38) = -87.77$ esu and thus, at 21 °C: $\Delta G°_f = 40.28$ Kcal·mol^{-1} = 1.747 eV; $\Delta G°_{f,Br^- \text{in DMF}} = -1.072 + 0.311 = 0.761$ eV.[6c] Thus, at the same temperature $E°$(Br>C—C<Br/·>C—C<Br + Br$^-$) = $\Delta G°_f$(Br>C—C<Br) − $\Delta G°_f$(·>C—C<Br) − $\Delta G°_f$(Br$^-$) − 0.183 = −0.875 V vs. SCE.

(19) (a) For example, the bond dissociation energy of a C–Cl bond in 1,2-dichloroethane[19b] is about 0.12 eV smaller than calculated assuming the validity of the additivity rule.[12b] (b) Goldfinger, P.; Martens, G. *Trans Faraday Soc.* **1961**, *57*, 2220.

(20) (a) $\Delta G^{\ddagger}_{\mathrm{hom}}$ and $\Delta G^{\ddagger}_0$ are the homogeneous activation and standard activation free energies, respectively, expressed in eV. (b) Z^{sol}, the homogeneous frequency collision, was taken as equal to $4.05.10^{11}$ M^{-1}·s^{-1} on the average.[16]

(21) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317.

activation free energy an ca. 20% contribution of solvent reorganization and an ca. 80% contribution of the change in nuclei configuration due to the carbon–bromine bond breaking.

We note incidentally, in the framework of this mechanism, that the second reduction has a very positive standard potential (around 1 V vs. SCE) much more positive than what was observed or can be guessed for the case of monohalides.[6] The reason for this is that, in the present case, electron transfer is accompanied by the expulsion of a second Br^- leading to the olefin, a much more stable compound than the alkyl carbanion formed in the case of monohalides.

As expected, the OEP free base belongs to the redox catalyst family since it also gives rise upon one-electron reduction to an aromatic anion radical. The metalloporphyrins fall into two categories: OEPZn and OEPCu behave as redox catalysts just as the aromatic organic compounds whereas OEPNi, OEPFe, and OEPCo give rise to a much more efficient catalysis. In terms of the controlling rate constant, the acceleration is by a factor of $1.2\ 10^2$, $2.5\ 10^3$, and $2.5\ 10^5$, respectively, as compared to the redox catalyst that would have the same standard potential. This clearly points to the concept that the mechanism, in these three cases, is different from a simple outer-sphere[22] electron transfer bond breaking concerted process.

It is tempting to correlate these observations and the ability of the reduced metalloporphyrins to form a σ-alkyl complex upon reaction with an alkyl halide. This is well-known for cobalt[23] and iron[8a,24,25] porphyrins in keeping with the one-electron reduced state from Co(II) and Fe(II) existing predominantly as Co(I) and Fe(I) resonance forms. It is interesting to note, in this connection, that these porphyrins are able to catalyze, although slowly, the electrochemical reduction of aliphatic monohalides.[8b,26] On the opposite, the one-electron reduction complexes of Zn(II) and Cu(II) porphyrins have the physical properties of anion radicals.[27] The case of nickel is more ambiguous. No reaction of alkyl halides with one-electron reduced Ni(II) porphyrins has been reported so far. However, although this species has been viewed as a nickel(II)–porphyrin anion radical,[28a,b] there is recent ESR evidence that the contribution of the Ni(I) resonance form is significant.[28c] In the case of OEPNi, OEPFe, and OEPCo, we could thus envisage the transient formation of an α-bromoalkyl complex, along an S_N2 displacement mechanism, followed by a rapid expulsion of a second Br^- ion occurring either before or after the injection of a second electron. The latter would most probably occur in the solution rather than at the electrode surface in view of the values of the rate constants of the rate-determining step.[4] For steric reasons, this is not likely to occur with the axial–axial isomer of *trans*-1,2-dibromocyclohexane. However, the more favorable equatorial isomer slightly predominates at equilibrium in DMF, and the rates of interconversion between the two isomers are large.[9f]

It is not however possible to exclude, at present, another type of elimination that would involve Br abstraction by the Co(I), Fe(I), and Ni(I) complexes followed by or concerted with the expulsion of the second Br.[29] Further studies of the reaction involving a systematic investigation of electronic and steric effects are clearly warranted.

Experimental Section

Chemicals. The solvent, DMF, was vacuum distilled before use. The supporting electrolyte was Et_4NClO_4 twice recrystallized from ethylacetate–ethanol (95%) 2:1 mixtures. DBC and all catalysts were from commerical origin and used as received with the exception of OEPCu and OEPFeCl that were prepared according to previously described procedures.[30]

Instrumentation for cyclic voltammetry was the same as previously described.[31] The working electrode was a glassy carbon disk of 3-mm diameter carefully polished and ultrasonically washed before use and the reference electrode an aqueous NaCl saturated calomel electrode to which all potentials are referred throughout the paper.

For preparative scale experiments, we used a glassy carbon crucible of 35-mm diameter and 15-mm height as working electrode with 10 cm^3 solutions. The counter electrode was a magnesium wire[32] not separated from the catholyte. Magnesium is oxidized in the presence of the Br^- ions generated at the cathode before cyclohexene which avoids the anodic formation of DBC that would diffuse back to the cathode even in the presence of a separator such as a Nafion membrane. The cell was equipped with a reflux condenser in which methanol at −40 °C was circulated with a cold trap (methanol, −40 °C). The electrolysis products were analyzed by GC (20% FFAP on chromosorb for cyclohexene, 10% SE30 on PAW for DBC, temperature programmed between 80 and 230 °C).

Treatment of the Cyclic Voltammetry Kinetic Data. The standard potential and standard activation free energy derived from the DBC voltammograms as follows. Instead of referring the potential scale to the standard potential of the reaction,[10] we refer it to the middle between the half-peak and peak potentials. Thus the electrode potential is expressed as

$$E = E_{\mathrm{m}} + \Delta E$$

Thus, within the approximation that the transfer coefficient does not vary appreciably in the potential range comprised between the half-peak and the peak potentials

$$\Delta G^{\ddagger}_{\mathrm{el}} = \Delta G^{\ddagger}_{0,\mathrm{el}}\left[\left(1 + n\frac{E_{\mathrm{m}} - E^{\circ} - \phi_{\mathrm{r}}}{4\Delta G^{\ddagger}_{0,\mathrm{el}}}\right)^{2} + \frac{\Delta E}{2\Delta G^{\ddagger}_{0,\mathrm{el}}}\left(1 + n\frac{E_{\mathrm{m}} - E^{\circ} - \phi_{\mathrm{r}}}{4\Delta G^{\ddagger}_{0,\mathrm{el}}}\right)\right]$$

the transfer coefficient, α, being expressed in this potential range as

$$\alpha \simeq \alpha_{\mathrm{m}} = \frac{1}{2}\left(1 + n\frac{E_{\mathrm{m}} - E^{\circ} - \phi_{\mathrm{r}}}{4\Delta G^{\ddagger}_{0,\mathrm{el}}}\right)$$

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(22) Outer-sphere, from the point of view of the electrode or of the catalyst.

(23) (a) Dolphin, D.; Johnson, A. W. *Chem. Commun.* **1965**, 494. (b) Whitlock, H. W.; Bowers, B. K. *Tetrahedron Lett.* **1965**, 4827. (c) Momenteau, M.; Fournier, M.; Rougée, M. *J. Chim. Phys.* **1970**, *67*, 926. (d) Kobayashi, H.; Hara, T.; Kaisu, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2148. (e) Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97.

(24) (a) Cohen, I. A.; Ostfeld, D.; Lichtenstein, B. *J. Am. Chem. Soc.* **1972**, *74*, 4522. (b) Lexa, D.; Momenteau, M.; Mispelter, M. *Biochim. Biophys. Acta* **1974**, *338*, 151. (c) Kadish, K. M.; Larson, G.; Lexa, D.; Momenteau, M. *J. Am. Chem. Soc.* **1975**, *97*, 282. (d) Reed, C. A. *Adv. Chem. Ser.* **1982**, *201*, 333. (e) Mashiko, T.; Reed, C. A.; Haller, K. J.; Scheidt, W. R. *Inorg. Chem.* **1984**, *23*, 3192. (f) Srivatsa, G. S.; Sawyer, D. T.; Boldt, N. J.; Bocian, D. F. *Inorg. Chem.* **1985**, *24*, 2123. (g) Hickman, D. L.; Shirazi, A.; Goff, H. M. *Inorg. Chem.* **1985**, *24*, 563.

(25) Note that there is clear evidence[8a] that the alkylation of Fe(I) and Co(I) porphyrins by aliphatic monohalides proceeds along an S_N2 mechanism rather than by electron transfer followed by coupling of the resulting Fe(II) and Co(II) with the alkyl radical.

(26) (a) Hill, H. A. O.; Pratt, J. M.; Riordan, M. P.; Williams, F. R.; Williams, R. P. J. *J. Chem. Soc. A* **1971**, 1859. (b) Lexa, D.; Savéant, J. M.; Soufflet, J. P. *J. Electroanal. Chem.* **1979**, *100*, 159. (c) Lexa, D.; Savéant, J. M.; Soufflet, J. P. In *Vitamin B12*; Zagalak, B., Friedrich, W., Eds.; De Gruyter: Berlin, 1979, p 213. (d) Lexa, D.; Savéant, J. M. *Acc. Chem. Res.* **1983**, *16*, 235.

(27) (a) As established on ESR spectroscopy[27b] and electrochemical grounds.[27c] (b) Fajer, J.; Davis, M. S. In *Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 197–233. (c) Felton, R. H. In *Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. V, pp 70–81.

(28) (a) Rouse, C. A.; Iwamoto, R. T. *J. Electroanal. Chem. Bioelectrochem. Bioenerg.* **1983**, *156*, 359. (b) Chang, D.; Malinski, T.; Ulman, A.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 817. (c) Lexa, D.; Momenteau, M.; Savéant, J. M., unpublished results.

(29) (a) Goering, H. L.; Espy, H. H. *J. Am. Chem. Soc.* **1955**, *77*, 5023. (b) Goering, H. L.; Sims, L. L. *J. Am. Chem. Soc.* **1955**, *77*, 3465. (c) Stevens, C. L.; Valicenti, J. A. *J. Am. Chem. Soc.* **1965**, *87*, 838. (d) Kray, W. C., Jr.; Castro, C. E. *J. Am. Chem. Soc.* **1964**, *86*, 4603. (e) Kochi, J. K.; Singleton, D. M. *J. Org. Chem.* **1968**, *33*, 1027. (f) Kochi, J. K.; Singleton, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 1582. (g) Chock, P. E.; Halpern, J. *J. Chem. Soc.* **1969**, *91*, 582. (h) Wegner, P. A.; Delaney, H. S. *Inorg. Chem.* **1976**, *15*, 1918. (i) Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 218.

(30) (a) Paine, J. B., III. Kirshner, W. B.; Moskowitz, D. W.; Dolphin, D. *J. Org. Chem.* **1976**, *41*, 3857. (b) Fuhrhop, J. H.; Smith, K. M. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: p 798.

(31) (a) Croisy, A.; Lexa, D.; Momentau, M.; Savéant, J. M. *Organometallics* **1985**, *9*, 1574. (b) Lexa, D.; Momenteau, M.; Rentien, P.; Rytz, G.; Savéant, J. M.; Xu, F. *J. Am. Chem. Soc.* **1983**, *106*, 4755.

(32) Sibille, S.; Coulombeix, J.; Perrichon, J.; Fuch, J. M.; Mortreux, A.; Petit, F. *J. Mol. Catal.* **1985**, *32*, 239.

Thus the potential dependent forward rate constant of electron transfer, k, is related to the standard free energy of activation and to the collision frequency Z^{el} according to

$$\frac{RT}{F}\ln\frac{Z^{el}}{k} = \Delta G^{\ddagger}_{0,el}\left(1 + n\frac{E_m - E^\circ - \phi_r}{4\Delta G^{\ddagger}_{0,el}}\right)^2$$

and the current flowing through the electrode surface expressed as

$$\frac{i}{FS} = k\exp\left(-\frac{\alpha nF}{RT}\Delta E\right)(C_A)_0$$

(S, electrode surface area; $(C_A)_0$, concentration of the reactant at the electrode surface).

Let us introduce the dimensionless variables of potential and current

$$\xi = -\frac{\alpha nF}{RT}\Delta E + \ln\left[\frac{k}{\left(\frac{\alpha nFDv}{RT}\right)^{1/2}}\right],$$

$$\psi = \frac{i}{FSC^\circ\left(\left(\frac{\alpha nFvD}{RT}\right)\right)^{1/2}}$$

Thus[10]

$$\psi\exp(-\xi) = 1 - \frac{1}{\pi^{1/2}}\int_{-\infty}^{\xi}\frac{\psi(\eta)}{(\xi-\eta)^{1/2}}$$

which is the dimensionless expression of the voltammogram. At the peak, $\xi_p = 0.78$, and the width of the peak is $\xi_p - \xi_{p/2} = 1.85$.[10]

It follows that

$$\frac{RT}{F}\ln\left(\frac{Z^{el}}{k}\right) = \frac{RT}{F}\ln\left[\frac{Z^{el}}{\left(\frac{\alpha nFDv}{RT}\right)^{1/2}}\right] + 0.145\frac{RT}{F}$$

with

$$\Delta G^{\ddagger}_{0,el} = \frac{1}{4\alpha^2}\frac{RT}{F}\ln\left[\frac{Z^{el}}{k}\right] \quad \text{and}$$

$$E^\circ = E_m - \phi_r + \frac{4\Delta G^{\ddagger}_{0,el}(1-2\alpha)}{n}$$

The estimation of the uncertainty ranges on $\Delta G^{\ddagger}_{0,el}$ and E° is as follows:

$$\Delta(\Delta G^{\ddagger}_{0,el}) = \frac{1}{4\alpha^2}\frac{\Delta\alpha}{\alpha}\frac{RT}{F}\left(\frac{1}{2} + 2\ln\frac{Z^{el}}{k}\right)$$

Since

$$\Delta(E_{p/2} - E_p) \simeq \pm 5\text{ mV}$$

and thus

$$\frac{\Delta\alpha}{\alpha} = \frac{\Delta(E_{p/2} - E_p)}{E_{p/2} - E_p} = \pm 3.8\%$$

$$\Delta(\Delta G^{\ddagger}_{0,el}) \simeq \pm 50\text{ mV}$$

$$\Delta E^\circ = \Delta(E_m) + 8\Delta G^{\ddagger}_{0,el}\Delta\alpha + 4(1-2\alpha)\Delta(\Delta G^{\ddagger}_{0,el}) \simeq \pm 130\text{ mV}$$

The treatment of homogeneous catalysis data was slightly modified as compared to usual procedures[4] in order to take into account the possible interference at the level of the catalytic wave of the direct electrochemical reduction. The principle of the method is to introduce the kinetic characteristics of the direct reduction, as derived from a separate study, into the calculation as a boundary condition expressing how the substrate is reducible in the investigated potential range. When an important overlap between the catalytic and direct waves occurred, the voltammetric pattern may no longer exhibit a peak. This is the reason why we took, as observable, the catalytic current at a potential equal to the peak potential of the catalyst in the absence of substrate, rather than the catalytic peak current.

In the fitting of the $\log k_1 - E^\circ_{PQ}$ curve with the quadratic law using a given value of the E°, the range of uncertainty for the determination of $\Delta G^{\ddagger}_{0,hom}$ was found to be ±5 mV. The uncertainty on E° introduces an additional error of about ±75 mV on $\Delta G^{\ddagger}_{0,hom}$.

Conclusion

The above described results and discussion show, with the example of dissociative electron transfer to *trans*-1,2-dibromocyclohexane, that homogeneous catalysis of the same electrochemical reaction may follow two different mechanisms according to the chemical nature of the catalyst. With aromatic or heteroaromatic catalysts, a typical redox catalysis process is observed. The rate-determining step of the reaction as well as that of the direct electrochemical reduction at glassy carbon consists of the injection of an electron concerted with the breaking of a carbon–bromine bond leading to a ·>C—C<Br radical which is reduced in a successive step with cleavage of the second C–Br bond to give the final olefin. Injection of the second electron and/or expulsion of the second bromide ion are not concerted with the first electron transfer bond breaking process. The direct reduction and the redox-catalyzed reaction follows the same quadratic activation driving force free energy relationship involving two additive reorganization factors. The major one (80%) concerns bond breaking, being of the order of one fourth of the carbon–bromine bond dissociation energy, whereas the minor one (20%) concerns solvent reorientation. As compared to aromatic anion radicals, reduced metalloporphyrins (formally at the "I" oxidation state) fall into two categories. Zinc and copper porphyrins behave as aromatic radicals whereas nickel, iron, and cobalt porphyrins react much more rapidly than aromatic anion radicals that would have the same standard potential. A different mechanism then takes place which is likely to involve either the formation of a transient σ-alkyl complex decomposing spontaneously or after a second electron transfer to yield the final olefin or Br abstraction followed by or concerted with the elimination of the second Br.

Acknowledgment. Michel Momenteau (Institut Curie, Orsay, France) is thanked for the gift of OEPCu and OEPFe samples. The help of Claude Andrieux and Philippe Hapiot (Laboratoire d'Electrochimie Moléculaire de l'Université de Paris 7) in manipulating the thermodynamical data and treating the catalytic currents in the case of unequal diffusion coefficients is gratefully acknowledged.

Registry No. DBC, 7429-37-0; OEPNi, 24803-99-4; OEPFe, 61085-06-1; OEPZn, 17632-18-7; OEPCu, 14409-63-3; $OEPH_2$, 2683-82-1; OEPCo, 17632-19-8; benzo[*c*]chinoline, 229-87-8; terephthalonitrile, 623-26-7; perylene, 198-55-0; fluorenone, 486-25-9.