

detection of the resulting ions would provide molecular weight information. After collisional relaxation, these *same* ions could be dissociated and analyzed; large daughter ions could again be relaxed, dissociated, and detected to determine their structure (using the Hadamard technique²⁶ to increase sensitivity). Even a limited sequence can allow cloning of the unknown protein, while continuing the process exploiting the MSⁿ capabilities of FTMS

(26) Williams, E. R.; Loh, S. Y.; McLafferty, F. W.; Cody, R. B. *Anal. Chem.* 1990, 62, 698-703. For a single ionization event, the Hadamard technique could be implemented by storing ions in an elongated trap adjacent to the cell; a portion of these ions could be transferred into the cell for each Hadamard measurement.

should provide increasingly extensive sequence information concerning the original protein.

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Registry No. Gramicidin S, 113-73-5; gramicidin D, 1393-88-0; crystal violet, 548-62-9.

Outer-Sphere and Inner-Sphere Processes in Reductive Elimination. Direct and Indirect Electrochemical Reduction of Vicinal Dibromoalkanes

Doris Lexa,^{1a} Jean-Michel Savéant,^{*,1a} Hans J. Schäfer,^{*,1b} Khac-Binh Su,^{1a} Birgit Vering,^{1b} and Dan Li Wang^{1a}

Contribution from the Laboratoire d'Electrochimie Moléculaire de l'Université Paris 7, Unité Associée au CNRS N° 438, 2 place Jussieu, 75251 Paris, Cedex 05, France, and the Organisch-Chemisches Institut der Westfälischen Wilhelms Universität, Orléans Ring 23, 4400 Münster, FRG. Received October 24, 1989

Abstract: The reduction of vicinal dibromoalkanes is investigated as an example of the dichotomy between outer-sphere and inner-sphere processes in reductive elimination. As a result from the analysis of the kinetic data, outer-sphere reagents such as carbon electrodes and aromatic anion radicals react with vicinal dibromoalkanes according to an "ET" mechanism in which the rate-determining step is a concerted electron-transfer bond-breaking reaction leading to the β -bromoalkyl radical. The latter is then reduced very rapidly, in a second step, most probably along another concerted electron-transfer bond-breaking pathway leading directly to the olefin in the heterogeneous case and through halogen atom expulsion in the homogeneous case. In the absence of steric constraints, the reduction goes entirely through the antiperiplanar conformer because the resulting β -bromoalkyl radical is then stabilized by delocalization of the unpaired electron over the C-C-X framework due to a favorable interaction between the p_z orbital of the radical carbon and the σ^* orbital of the C-Br bond. This interaction is enhanced by alkyl substitution at the reacting carbons, resulting in an approximately linear correlation between the reduction potential and the C-X bond energy of OIX₂ on one hand and the vertical ionization potential of the olefin on the other. The stabilization energy is of the order of 0.2-0.3 eV for the anti conformers. It can also be taken as a measure of the rotation barrier around the C-C bond responsible for the loss of stereospecificity in the reduction. This competes with the reduction of the two stable conformers of the OIX^{*} radicals and for the expulsion of the halogen atom. There is a remarkably good agreement between the ensuing prediction of the *E:Z* olefin ratio that should be found upon reduction of threo and erythro OIX₂ isomers by outer-sphere reagents such as aromatic anion radicals and the experimental data. Although members of perfectly reversible redox couples, iron(I), iron("0"), and cobalt(I) porphyrins offer typical examples of inner-sphere reagents in their reaction with vicinal dibromoalkanes. They indeed react much more rapidly than outer-sphere electron donors (aromatic anion radicals) of the same standard potential. On the basis of steric hindrance experiments, it was shown that they do not react according to an S_N2 rate-determining step involving the transient formation of an organometallic species. Complete stereospecificity is obtained, showing that they react along a halonium transfer E2 elimination mechanism rather than by an E1 elimination or a halogen atom transfer mechanism. As shown on a quantitative basis, this is related to the large driving force offered to halonium abstraction by the strong affinity of the iron(III) and cobalt(III) complexes toward halide ions. In regards to catalysis, the investigated systems provide typical examples showing the superiority of inner-sphere (chemical) catalysis over outer-sphere (redox) catalysis of electrochemical reactions. Not only is the catalytic efficiency much better since the rate constants of the key steps are larger, given the standard potential of the catalyst, but also selectivity is dramatically improved.

The discovery of substitution reactions involving radical anion intermediates at aliphatic^{2a,b} and aromatic^{2c} carbons (S_{RN}1 reactions) as well as the development of synthetic, mechanistic, and kinetic studies in organic electrochemistry³ has drawn active

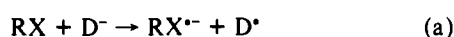
attention to the role of single electron transfer—as opposed to electron pair transfer—in organic chemistry. The mechanism of the S_{RN}1 reaction is now reasonably well understood,⁴ even at the

(1) (a) Université de Paris 7. (b) Westfälische Wilhelms-Universität.
(2) (a) Kornblum, N.; Michel, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* 1966, 88, 5662. (b) Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* 1966, 88, 5663. (c) Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* 1970, 92, 7463.

(3) See, for example: (a) *Organic Electrochemistry*; Baizer, M. M., Lund, H., Eds.; Marcel Dekker: New York, 1983. (b) Andrieux, C. P.; Savéant, J.-M. *Electrochemical Reactions in Investigation of Rates and Mechanisms of Reactions, Techniques of Chemistry*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. VI/4E, Part 2, pp 305-390.

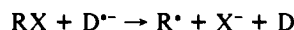
quantitative level in the case of aromatic centers thanks to the electrochemical approach of the problem.^{4d,f,g} The reaction proceeds by means of a chain mechanism in which the electrons play the role of a catalyst. The species that reacts with the nucleophile is not the substrate itself but rather the aryl radical derived from its anion radical by expulsion of the leaving group. Single electron transfer is involved in the generation of the anion radical of the substrate by means of an initiator and also in the reoxidation of the anion radical of the substituted product by the substrate which propagates the chain. The termination steps have been identified, and the rate constant of the coupling of the aryl radical with the nucleophile has been determined in a number of instances.

Of different nature is the problem of the possible involvement of single electron transfer in reactions that are not catalyzed by electron injection (or removal). The question which then arises is to know whether or not reactions that so far have been considered to proceed by electron pair transfer in fact involve single electron transfer. In this respect, S_N2 substitution has attracted particular attention.⁵ The problem amounts to distinguishing between stepwise and concerted electron transfer, bond breaking, and bond formation

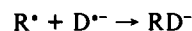


and is most conveniently discussed in terms of outer-sphere vs inner-sphere processes. The outer-sphere/inner-sphere terminology has been coined for reactions involving coordination complexes.^{6a,b} It can, however, be extended to organic processes.^{5h} In outer-sphere electron-transfer reactions, either no bond is cleaved or formed within the time scale of the experiment or, in the opposite case, bond breaking and bond formation take place in separate steps, distinct from the electron-transfer step. Thus, if reactions (a)–(c) occur stepwise, the overall substitution reaction, $\text{RX} + \text{D}^- \rightarrow \text{RD} + \text{X}^-$, proceeds by means of outer-sphere electron transfer.⁷ Conversely if they are all concerted, we deal with an inner-sphere electron transfer. An S_N2 substitution reaction may thus be considered as formally equivalent to an inner-sphere electron-transfer reaction.⁸ With an alkyl halide, a common electrophile (electron acceptor) in S_N2 reactions, steps (a) and

(b) are concerted even with outer-sphere electron donors such as inert electrodes or aromatic anion radicals.⁹



The reaction has thus an outer-sphere character from the point of view of the donor but an inner-sphere character from that of the acceptor.^{9d} Note that in the case of aromatic anion radicals, bond formation occurs by coupling between R[•] and the electron donor

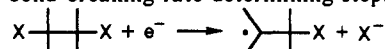


rather than with D.

The preceding pathways are not the only conceivable routes to substitution. Halogen-atom abstraction followed by coupling between the R and D moieties have also been observed, for example, in the case of alkyl halides and transition-metal complexes^{10a} and with trifluoromethyl bromide and SO₂^{•-} radicals.^{10b,c}

Similar questions arise for reductive elimination, and vicinal dihalides may serve as an example for the alkyl monohalides in the case of nucleophilic substitution. As was made clear in the following discussion, the main inner-sphere reactions that are to be taken into consideration, however, now involve the halogens rather than the functional carbons, whereas outer-sphere reducing agents may well react along the same rate-determining pathway as in the case of monohalides.

Electrochemical reduction of vicinal dihalides is a facile and quantitative route to the parent olefins at mercury,¹¹ carbon,^{12a,b} and platinum^{12c} electrodes. Cathodic debromination has been used for the selective protection of differently substituted double bonds in dienes.^{11e,f} Debromination can also be achieved in indirect electrochemical reductions by using electrogenerated aromatic anion radicals^{11,12a,b} as reducing agents as shown in the case of 1,2-dichloro- and 1,2-dibromo-1,2-diphenylethanes^{11d} and *trans*-1,2-dibromocyclohexane.^{12a,b} The same is also true when low oxidation states of metalloporphyrins are used as electron donors as shown in the case of 1,2-dibromocyclohexane.^{12a,b} Concerning the latter compound, it has been shown that the heterogeneous kinetic data (at a glassy carbon electrode) as well as those pertaining to the reduction by electrogenerated aromatic anion radicals can be rationalized in the context of a concerted electron-transfer bond-breaking rate-determining step:



the electrode and the aromatic anion radicals thus reacting in an outer-sphere manner, as in the case of alkyl monohalides. The ensuing β-halogenated alkyl radical is further converted into the olefin in a successive reaction involving the uptake of a second

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(8) (a) Even more than formally in several instances where the D^{•-}:R[•]X and D^{•-}:X[•] valence bond configurations predominate over the other possible configurations in the description of the potential energy surfaces.^{8bc} “Electron shift”^{8bc} and inner-sphere electron transfer are then equivalent concepts. (b) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99. (c) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 187.

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(12) (a) Lexa, D.; Savéant, J.-M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 6464. (b) The first entry of Table III in ref 12a was omitted in printing. It should read from left to right: direct reduction, reduction potential, –1.87; DBC concentration; 14.6 mM; number of electrons, 1.85; cyclohexane yield, 97.2%. (c) Brown, O. R.; Middleton, P. H.; Threlfall, T. L. *J. Chem. Soc., Perkin Trans. 2* **1984**, 955. (d) Solvated electrons electrochemically generated in liquid ammonia have also been used to reduce 3,4-dibromohexane and 2,5-dimethyl-3,4-dibromohexane into the corresponding olefins.^{12c}

electron and the loss of the second halide ion.^{13a} Cobalt(I), iron(I), and nickel(I) porphyrins^{12a,13b-c} react much more rapidly than outer-sphere reagents (i.e., aromatic anion radicals) having the same standard potentials. These electron donors, although members of perfectly reversible redox couples, do not react with *trans*-1,2-dibromocyclohexane in an outer-sphere manner thus pointing to the existence of bonding interactions in the transition state.^{12a,14}

Besides kinetics, the stereochemistry of reductive elimination is an important clue to its mechanism. One series of stereochemical factors that control the course of the reaction is the conformational arrangement of the two halogens. Investigation of the electrochemical reduction of various vicinal dibromocycloalkanes having a blocked conformation on a mercury electrode has shown that the molecules possessing an anti arrangement of the two bromines are significantly easier to reduce than any others.^{15a,b} One example of the same behavior has been found with another electrode material, namely platinum.^{15b,16} On the basis of this observation, a thorough study of the conformational changes preceding electron transfer to cyclic and acyclic vicinal dibromides with unblocked conformational structures has been carried out on mercury and platinum electrodes:^{15b-d} the anti conformer being first reduced, depending upon temperature, a more or less important part of the reduction of the other conformers goes through their prior conversion into the anti conformer.

Another important mechanism revealing aspect of the stereochemistry of reductive elimination in vicinal dihaloalkanes concerns the relative amount of *Z* and *E* olefins obtained upon reduction of *threo*- and *erythro*-dihaloalkanes. The reduction of *meso*- and *dl*-2,3-dibromobutanes on mercury is remarkably stereospecific since they quantitatively yield the *trans*- and *cis*-2-butene, respectively.^{11b} The situation is less straightforward with the reduction, also on mercury, of 1,2-dihalo-1,2-diphenylethanes.^{11c,d} The *meso*-dibromo and -dichloro derivatives as well as the *dl*-dichloro isomer give exclusively *trans*-stilbene, whereas *dl*-1,2-dibromo-1,2-diphenylethane gives a mixture of *cis*- and *trans*-stilbenes, the composition of which is a function of the concentration and of the cation of the supporting electrolyte. Reduction of *meso*- and *dl*-3,4-dibromohexane and 3,4-dibromo-2,5-dimethylhexane, in DMF or in liquid ammonia, at platinum or gold electrodes, yields mixtures of the corresponding *trans*- and *cis*-olefins in proportions that are depending upon the electrolysis potential.^{12c} Under "mild" electrolysis conditions, i.e., at not too negative potentials, complete stereospecificity was observed.¹⁶

Indirect reduction of 1,2-dihalo-1,2-diphenylethanes by means of aromatic anion radicals^{11d} gave quantitatively the *trans*-olefin with the above first three derivatives as in the direct reduction

on mercury, whereas *dl*-1,2-dibromo-1,2-diphenylethanes gave a small amount (7%), smaller than in the reduction on mercury, of the *cis*-olefin. Chemically prepared aromatic anion radicals, such as alkali naphthalenes, also convert quantitatively vicinal dihaloalkanes into the corresponding olefins.¹⁷ *Meso*- and *dl*-2,3-dichlorobutanes lead to the same *trans*-/*cis*-2-butenes mixture in which the *trans*-olefin largely predominates.^{17c,d} This is not the case with the corresponding dibromo derivatives. The *meso* derivative gives more *trans*- and less *cis*-butene than the *dl* derivative.^{17c} Similar trends are observed with *threo*- and *erythro*-2,3-dibromo-2,3-methylpentanes.^{17b} It is also interesting to note that the reduction of *meso*- and *dl*-3,4-dibromohexane by solvated electrons in liquid ammonia leads to the same equilibrium mixture of *trans*- and *cis*-3-hexenes.^{12c}

A very large number of other reagents have been shown to bring about vicinal dehalogenation reactions,¹⁸⁻²¹ whether they react in an outer-sphere or inner-sphere manner. The stereochemistry is nonselective in most cases. However, iodide^{21a,c} and trialkylstannate^{20c} ions offer two remarkable examples of stereospecificity: *meso*- and *dl*-2,3-dibromobutanes are converted quantitatively into *trans*- and *cis*-2-butenes, respectively.

The purpose of the work reported hereafter was to get a better understanding of outer-sphere and inner-sphere electron transfers in reductive elimination, to evaluate how the differences between these two types of mechanisms manifest themselves, and to identify the factors that control their occurrence. The discussion will thus deal with three main possible mechanisms involving the following rate-determining steps:^{22a}

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(19) Metals, such as alkali metals,^{19a-c,e} magnesium,^{19d-f} zinc,^{19d-f} cadmium,^{19b,e} and transition-metal complexes such as Fe(II),^{19f} Co(II),^{19a,h} Cr(II),^{19d-g,19i-k} Sn(II),^{19l,n} Ti(II),^{19f} Pt(II),^{19f} Fe(CO)₂CpNa,^{19o} and Rh(I) tetraazamacrocycles:^{19p} (a) Schubert, W. M.; Rabinovitch, B. S.; Larson, N. R.; Sims, V. A. *J. Am. Chem. Soc.* **1952**, *74*, 4590. (b) House, H. O.; Ro, R. S. *J. Am. Chem. Soc.* **1958**, *80*, 182. (c) Allred, E. A.; Beck, B. R.; Voorhees, K. J. *J. Org. Chem.* **1974**, *39*, 1426. (d) Amstutz, E. D. *J. Org. Chem.* **1944**, *9*, 310. (e) Sicher, J.; Havel, M.; Svoboda, M. *Tetrahedron Lett.* **1968**, 4269. (f) Mathai, I. M.; Schug, K.; Miller, S. I. *J. Org. Chem.* **1970**, *35*, 1733. (g) Halpern, J.; Maher, J. P. *J. Am. Chem. Soc.* **1945**, *67*, 5361. (h) Kray, W. C.; Castro, C. E. *J. Am. Chem. Soc.* **1964**, *86*, 4603. (i) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 582. (j) Singleton, D. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1967**, *89*, 6547. (k) Singleton, D. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1968**, *90*, 1582. (l) Kochi, J. K.; Singleton, D. M.; Andrews, L. J. *Tetrahedron Lett.* **1968**, *24*, 3503. (m) Wegner, P. A.; Delaney, M. S. *Inorg. Chem.* **1976**, *15*, 1918. (n) Kwok, W. K.; Miller, S. I. *J. Am. Chem. Soc.* **1970**, *92*, 4599. (o) McMurry, J. E.; Hoz, T. *J. Org. Chem.* **1975**, *40*, 3795. (p) Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 218.

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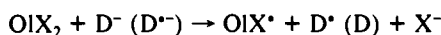
(13) (a) Whether the second electron is injected first and the X⁻ anion then expelled or, vice versa, X⁻ is cleaved first, and the ensuing cation radical then reduced is not known. The two steps may also be concerted. This in fact appears as the most likely mechanism in view of the strong driving force offered by the formation of the parent olefin.^{12a} (b) Octaethylporphyrins (OEP). (c) Reduced zinc and copper OEPs behave as aromatic anion radicals as also does the reduced OEP free base.^{12a} (d) Electrochemically generated vitamin B_{12a} has been also shown to catalyze the reduction of 1,2-dibromothane and butane.^{13a} (e) Connors, T. F.; Arena, J. V.; Rusling, J. F. *J. Phys. Chem.* **1988**, *92*, 2810.

(14) (a) Rate data are also available for the reduction of *meso*- and *dl*-1,2-dichloro-1,2-diphenylethanes by aromatic anion radicals.^{14b} It is interesting to note for the discussion below that a carbanion, viz., the anion of 1,4-dihydro-4-(methoxycarbonyl)-1-methylpyridine, behaves as an aromatic anion radical having the same standard potential,^{14b} in contrast with what was previously observed in the reaction with alkyl monohalides where its reactivity was significantly larger.^{5d} (b) Lund, T.; Pedersen, S. U.; Lund, H.; Cheung, K. W.; Utey, J. H. P. *Acta Chem. Scand. B* **1987**, *41*, 285.

(15) (a) Zavada, J.; Krupicka, J.; Sicher, J. *Coll. Czechoslov. Chem. Commun.* **1963**, *28*, 1664. (b) O'Connell, K. M.; Evans, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 1473. (c) Klein, A. J.; Evans, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 757. (d) Evans, D. H.; O'Connell, K. M. *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1986; pp 113-207. (e) Bowyer, W. J.; Evans, D. H. *J. Electroanal. Chem.* **1988**, *240*, 227.

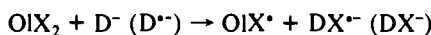
(16) Reduction of *vic*-dihalides on mercury, and to a lesser extent, on platinum and gold, appears easier than on glassy carbon.^{12a,c,15b,c} This seems to indicate that glassy carbon is the closest model of an heterogeneous outer-sphere electron donor, whereas mercury and possibly platinum and gold would work as inner-sphere heterogeneous electron donors.

outer-sphere electron transfer (ET)^{22b,c}



and two possible inner-sphere electron-transfer mechanisms^{22d}

halogen-atom transfer (HA)^{22c}



halonium ion transfer concerted with halide expulsion

(E2 elimination)^{22c-h}



The glassy carbon electrode and aromatic anion radicals will be taken as examples of outer-sphere reagents, whereas iron(I), iron⁰(0), and cobalt(I) porphyrins will serve as examples of inner-sphere reagents. The reduction at a mercury electrode will also be examined briefly. The rate data for the electrochemical reactions were obtained from cyclic voltammetry (at glassy carbon) or differential pulse polarography (at mercury). The rate constants for the reaction with the homogeneous electron donors were measured from the catalytic increase of the cyclic voltammetric reversible wave of the parent compound^{3b,23} (at a glassy carbon electrode) upon adding the vic-dibromoalkanes. Our strategy for gathering more information on the electronic and steric effects governing the reactivity of the above-mentioned outer-sphere and inner-sphere reagents with vicinal dibromides involved the following set of experiments.

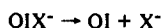
1. The antiperiplanar preference of the reaction with outer-sphere and inner-sphere reagents was investigated by measuring the rate constants for the reaction of blocked axial-axial and equatorial-equatorial dibromocyclohexanes with glassy carbon and mercury electrodes as well as with aromatic anion radicals and iron(I) and cobalt(I) porphyrins.²⁴

2. Electronic effects were examined by determining the electrochemical characteristics of an extended series of acyclic dibromides bearing various alkyl substituents at the functional

(22) (a) OIX₂, OIX[•], and OI stand for *††x, ††x, and ††x respectively. D^{•-} and D[•] represent electron donors possessing or not possessing an unpaired electron, respectively. Thus, D^{•-} will stand for aromatic anion radicals and iron(I) porphyrins, whereas D[•] denotes cobalt(I) and iron⁰(0) porphyrins even though the latter bears two negative charges. (b) In this case, as previously noted, electron transfer possesses outer-sphere character from the standpoint of the electron donor but inner-sphere character from the standpoint of the vicinal dihalide, since the carbon-halogen bond is cleaved concertedly with electron transfer. (c) The olefin is successively formed by uptake of an electron from D^{•-} (D^{•-}) and cleavage of the second halide ion.^{13a} (d) The possibility of an S_N2 attack at one of the functional carbons will also be discussed. (e) Still another "E" pathway is conceivable



followed by



However, the driving force for the E1 rate-determining step is much weaker than for the E2 rate-determining step owing to the largely downhill character of the reaction OIX^{•-} → OI + X⁻. (f) E2 and E1 can also be viewed as an S_N2 nucleophilic attack at the X carbon.^{22a} (g) Zefirov, N. S.; Makhon'kov, D. I. *Chem. Rev.* **1982**, *82*, 615. (h) Followed by the reduction of DX (DX[•]) by D^{•-}(I)^{•-}.

(23) (a) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *87*, 39. (b) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *87*, 55. (c) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *88*, 43. (d) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3431. (e) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 3806. (f) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1980**, *113*, 1. (g) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Electroanal. Chem.* **1980**, *113*, 19. (h) Savéant, J. M.; Su, K. B. *J. Electroanal. Chem.* **1984**, *171*, 341. (i) Andrieux, C. P.; Hapiot, P.; Savéant, J. M. *J. Electroanal. Chem.* **1985**, *189*, 121.

(24) 3(a),4(a)-Dibromo-1(e)-methylcyclohexane and 3(e),4(e)-dibromo-1(e)-methylcyclohexane were used for this purpose. As shown previously,^{15b} the first of these behaves, in slow scan cyclic voltammetry at room temperature, like the axial-axial isomer and the second like the equatorial-equatorial isomer with negligible interference of the other form for thermodynamic and kinetic reasons.

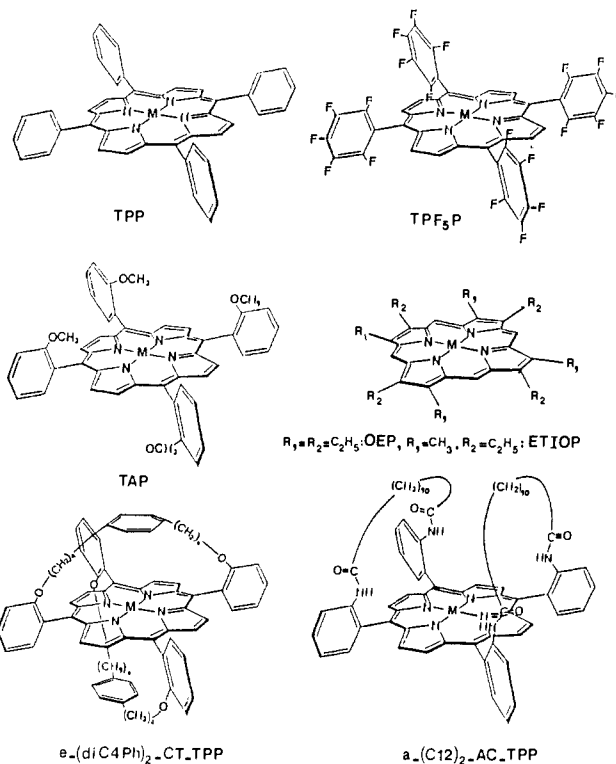


Figure 1. Porphyrins used in the present work with their conventional designations.

carbons on glassy carbon and mercury. The reactivity of the four most typical compounds in the series toward aromatic anion radicals and iron(I) and cobalt(I) porphyrins was also investigated.

3. The stereochemistry of the reaction was investigated by examining the stereospecificity of the reaction of *meso*- and *dl*-4,5-dibromooctanes with the same homogeneous reagents as well as with glassy carbon and mercury electrodes.

4. Additional electronic and stereochemical effects were examined by determining the rate constant of the reaction of *trans*-1,2-dibromocyclohexane with several other iron(I) and cobalt(I) porphyrins having different M(II)/M(I) standard potentials than the previously investigated OEP complexes.^{12a} The effect of steric hindrance at the metal center was investigated by using a sterically congested iron(I) basket-handle porphyrin as the electron donor. The same experiment was also carried out with dibromoethane. The reactivity of one iron⁰(0) porphyrin (having a standard potential close to that of OEPFe(I)) was also determined.

Results

The kinetic data featuring the direct electrochemical reduction, on glassy carbon and mercury in dimethylformamide, of a series of 16 vicinal dibromoalkanes are listed in Table I (second to fourth columns). Cyclic voltammetry was used with glassy carbon and differential pulse polarography with mercury. In the latter case, the half-wave potential was determined in the usual way. In the former, an irreversible two-electron wave was obtained with all investigated compounds. The potential, E_m , the values of which are given in Table I for a scan rate of 0.1 V s⁻¹, is the midpoint between the peak and half-peak potentials:


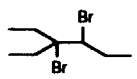
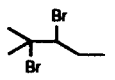
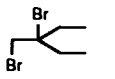
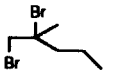
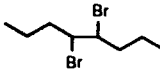
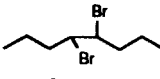
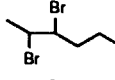
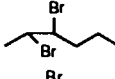

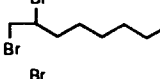
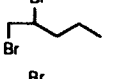

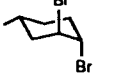
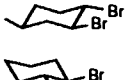
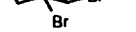
$$E_m = \frac{E_p + E_{p/2}}{2}$$

The transfer coefficient, α_m , at the potential E_m , was obtained from^{3b,12a}

$$\alpha_m = \frac{RT}{nF} \frac{1.85}{E_{p/2} - E_p}$$

n , being the number of electrons transferred in the rate-determining step. Due to a slight irreproducibility of the surface state

Table I. Direct Electrochemistry of Vicinal Dibromoalkanes^a and Treatment of Kinetic Data Obtained for Reduction at Glassy Carbon and by Electrogenerated Aromatic Anion Radicals^b

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
															glassy carbon ^c
dibromoalkane	E_m^e	$n\epsilon_m$	$E_{1/2}^e$	$E^{\circ e}$	$E^{\circ}_{1, \text{pred}}^e$	$E^{\circ}_{2, \text{pred}}^e$	$E^{\circ}_{\text{pred}}^e$	$D^{\circ}_{\text{cat}}^f$	$D^{\circ}_{\text{ct}}^f$	$\Delta G^{\ddagger}_{0, \text{el}}^f$	α_m^{th}	$E^{\circ}_{1, \text{th}}^e$	$D^{\circ}_{\text{hom}}^f$	I^f	
2,3-dibromo-2,3-dimethylbutane 	1	-1.439	0.38	-0.90	0.207	-0.53	0.84 (2.17)	2.44	2.78	2.39 (0.41)	0.73	0.35	-0.57	2.42	8.27
3,4-dibromo-3-ethylhexane 	2	-1.514	0.32	-1.16	0.173	-0.61	0.85 (2.35)	2.37	2.78	2.43 (0.35)	0.74	0.35	-0.61		8.48
2,3-dibromo-2-methylpentane 	3	-1.583	0.34	-1.25	0.173	-0.68	0.91 (2.47)	2.30	2.78	2.47 (0.31)	0.75	0.35	-0.65		8.62
1,2-dibromo-2-ethylbutane 	4	-1.681	0.33	-1.44	0.138	-0.78	0.94 (2.84)	2.20	2.78	2.54 (0.24)	0.76	0.34	-0.72	2.54	9.06
1,2-dibromo-2-methylpentane 	5	-1.702	0.33	-1.46	0.138	-0.80	0.96 (2.86)	2.18	2.78	2.55 (0.923)	0.77	0.34	-0.73		9.08
<i>meso</i> -4,5-dibromooctane 	6	-1.744	0.35	-1.57	0.138	-0.84	1.01 (2.65)	2.14	2.99	2.57 (0.42)	0.77	0.34	-0.75		8.83
<i>dl</i> -4,5-dibromooctane 	7	-1.844	0.35	-1.69	0.138	-0.94	1.01 (2.65)	2.04	2.99	2.62 (0.37)	0.79	0.34	-0.80		8.84
<i>erythro</i> -2,3-dibromohexane 	8	-1.736	0.36	-1.51	0.138	-0.83	1.00 (2.76)	2.14	2.99	2.57 (0.42)	0.79	0.34	-0.80		8.97
<i>threo</i> -2,3-dibromohexane 	9	-1.790	0.37	-1.63	0.138	-0.89	1.05 (2.76)	2.09	2.9	2.60 (0.39)	0.78	0.34	-0.78		8.97
2,3-dibromobutane 	10	-1.804	0.35	-1.51	0.138	-0.90	1.07 (2.90)	2.08	2.99	2.61 (0.38)	0.79	0.34	-0.79		9.13
1,2-dibromooctane 	11	-1.835	0.35	-1.65	0.136	-0.93	1.09 (3.13)	2.04	2.96	2.63 (0.33)	0.79	0.34	-0.81	2.64	9.40
1,2-dibromopentane 	12	-1.852	0.35	-1.63	0.136	-0.95	1.11 (3.06)	2.03	2.96	2.64 (0.32)	0.80	0.34	-0.82		9.52
1,2-dibromoethane 	13	-1.907	0.35	-1.67	0.134	-1.00	1.16 (4.07)	1.97	2.96	2.64 (0.32)	0.80	0.33	-0.85	2.68	10.50
3(a),4(a)-dibromo-1(e)-methylcyclohexane 	14	-1.736	0.37	-1.40	0.125	-0.83	0.97 (2.75)	2.14	2.94	2.56 (0.38)	0.77	0.34	-0.74	2.55	
3(e),4(e)-dibromo-1(e)-methylcyclohexane 	15	-2.195	0.31	-2.35	0.125	-1.23	1.62 (2.75)	1.69	2.94	2.35 (0.09)	0.84	0.32	-1.03	2.80	
<i>trans</i> -1,2-dibromocyclohexane 	16	-1.774	0.35	-1.51	0.125	-0.87	1.01 (2.75)	2.11	2.94	2.57 (0.37)	0.78	0.34	-0.75	2.58	8.95

^a In DMF at 20 °C. ^b For definitions of symbols see text. ^c Supporting electrolyte: 0.1 M Et₄NClO₄. ^d Supporting electrolyte: 0.1 M Bu₄NBF₄. ^e In V vs SCE. ^f In eV.

Table II. Rate Constants for the Reaction of Electrogenerated Aromatic Anion Radicals and Low Oxidation State Metalloporphyrins with Acyclic *vic*-Dibromoalkanes^a

dihaloalkane ^b	electrogenerated electron donor		log <i>k</i> ^d
	from	standard potential ^c	
1	1,4-diacetylbenzene	-1.413	4.15
	TPPZn ^{II}	-1.280	4.28
	9-fluorenone	-1.227	3.41
	TPPCu ^{II}	-1.141	3.63
	OEPFe ^{II}	-1.203	6.1
	OEPCo ^{II}	-0.970	6.1
4	phthalonitrile	-1.577	4.83
	tetraphthalonitrile	-1.504	4.15
	1,4-diacetylbenzene	-1.413	3.36
	OEPFe ^{II}	-1.203	5.51
10	OEPCo ^{II}	-0.970	5.36
	perylene	-1.620	5.00
	OEPFe ^{II}	-1.203	4.98
11	1-cyanonaphthalene	-1.810	5.35
	4-cyanopyridine	-1.734	4.11
	phthalonitrile	-1.577	3.73
	terephthalonitrile	-1.504	3.36
	OEPFe ^{II}	-1.203	4.85
	OEPCo ^{II}	-0.970	5.65
13	perylene	-1.620	3.84
	benzo[<i>c</i>]quinoline	-1.450	1.78
	9-fluorenone	-1.227	1.30
	OEPFe ^{II}	-1.203	5.04
	e-(diC ₄ Ph) ₂ -CT-TPPFe ^{II}	-1.070	5.66
	OEPCo ^{II}	-0.970	4.78

^a In DMF + 0.1 M Et₄NClO₄ at 20 °C. ^b For definitions see Table I. ^c In V vs SCE. ^d *k*, rate constant in M⁻¹ s⁻¹.

rather than to inaccuracy in potential measurements, the precision on the determination of E_m is about ± 5 mV and ± 0.025 on the determination of α_m . Values of α_m falling in the same uncertainty range were also derived from the variation of E_m with the sweep rate between 0.1 and 2.0 V s⁻¹.

The rate constants for the reaction of four of the previous 12 acyclic *vic*-dibromides with aromatic anion radicals (including reduced zinc(II) and copper(II) porphyrins as well as with iron(I) and cobalt(I) porphyrins are listed in Table II (the various porphyrins used in the present work are shown in Figure 1). Similar data pertaining to the three dibromocyclohexanes are listed in Table III. They were derived from the catalytic currents^{3b} obtained at the initially reversible wave of the parent compound upon addition of the dibromoalkane to the solution. In all cases, catalytic currents that corresponded to two electrons transferred on the overall from the donor to the dibromide^{3b,23} were observed. Derivation of the rate constant for the reaction of the electrogenerated electron donor with the dibromoalkane was carried out along known procedures.^{3b,12a,23}

In order to further characterize the differences between outer-sphere and inner-sphere reagents, we investigated the temperature dependence of the rate constant of the reaction of **14** with OEPFe(I) and with an aromatic anion radical, viz. perylene, which has about the same rate constant at room temperature. The ensuing Arrhenius plots are shown in Figure 2.

Besides the investigation of the dibromides **14** and **15**, the stereochemistry of the reaction was examined by determining the respective yields of *E* and *Z* olefins obtained upon direct electrolysis of *meso*- and *dl*-4,5-dibromooctane at a carbon and at a mercury electrode and indirect electrolysis using the 1,4-diacetylbenzene anion radical, OEPFe(I), and OEPCo(I) as catalysts. The results are displayed in Table IV. Some 4-bromo-4-octene was obtained together with the (*E*)- and (*Z*)-octenes, presumably arising from the production of electrogenerated bases from impurities. This, however, does not affect the *E*:*Z* ratio produced from the starting dibromooctanes, since the 4-bromo-4-octene is reduced at a much more negative potential (peak potential at glassy carbon: -2.83 V vs SCE at 0.1 V/s for the *Z* isomer) than the potentials applied in the electrolyses. ETIO-PCo was used as a representative of cobalt porphyrins instead of OEPCo for solubility reasons. Its electron donor properties are

Table III. Rate Constants for the Reaction of Electrogenerated Aromatic Anion Radicals and Low Oxidation State Metalloporphyrins with *vic*-Dibromocyclohexanes^a

dihaloalkane ^b	electrogenerated electron donor		log <i>k</i> ^d
	from	standard potential ^c	
14	perylene	-1.620	4.30
	OEPCu ^{II}	-1.430	3.76
	9-fluorenone	-1.227	1.83
	OEPFe ^{II}	-1.203	5.80
	OEPCo ^{II}	-0.970	5.40
15	anthracene	-1.905	4.57
	1-cyanonaphthalene	-1.810	4.00
	perylene	-1.620	2.72
16	OEPFe ^{II}	-1.203	2.81
	OEPCo ^{II}	-0.970	2.94
	perylene	-1.620	4.70 ^e
	OEPZn ^{II}	-1.560	4.28 ^c
	terephthalonitrile	-1.504	3.76 ^e
	benzo[<i>c</i>]quinoline	-1.450	2.79 ^e
	OEPCu ^{II}	-1.430	3.46 ^e
	OEPNi ^{II}	-1.350	4.77 ^e
	OEPH ₂	-1.293	2.02 ^e
	9-fluorenone	-1.227	2.00 ^e
	OEPFe ^{II}	-1.203	5.04 ^e
	TPF ₃ PFe ^I	-1.190	3.8
e-(diC ₄ Ph) ₂ -CT-TPPFe ^{II}	-1.070	3.49	
TAPFe ^{II}	-1.055	3.90	
TPPFe ^{II}	-0.986	3.60	
a-(C12) ₂ -AC-TPPFe ^{II}	-0.896	3.25	
OEPCo ^{II}	-0.970	5.20 ^e	
TPPCo ^{II}	-0.744	3.90	

^a In DMF + 0.1 M Et₄NClO₄ at 20 °C. ^b For definitions see Table I. ^c In V vs SCE. ^d *k*, rate constant in M⁻¹ s⁻¹. ^e From ref 12a.

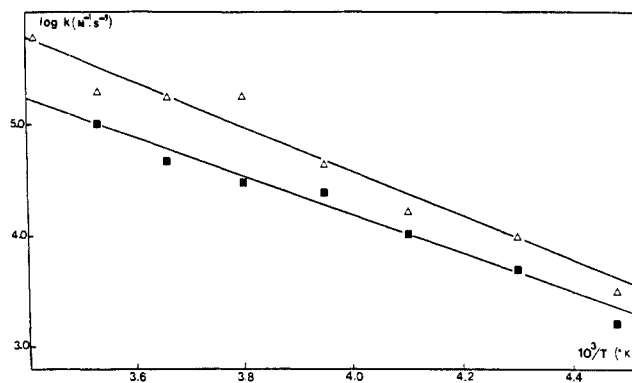


Figure 2. Arrhenius plots for the reaction of **14** with OEPFe^I (Δ) and perylene anion radical (\blacksquare).

close to those of OEPCo (standard potential of the Co(II)/Co(I) couple: -1.00 V vs SCE).

Discussion

In the whole series of vicinal dibromoalkanes, the electrochemical reduction on mercury appears significantly easier, by 200–500 mV in terms of overpotential, than on carbon (Table I). Similarly, the homogeneous reduction is much faster with iron(I), iron(0), and cobalt(I) porphyrins than with aromatic anion radicals (see Tables II and III and Figures 3 and 4, that represent the variations of the rate constant with the standard potential of the electron donor redox couple). As noted earlier,^{12a} reduced zinc(II) and copper(II) porphyrins behave as aromatic anion radicals in the sense that their representative points fall on the same activation vs driving force (i.e., log *k* vs standard potential) line as the aromatic anion radicals (Figures 3 and 4).

These are the first indications that the carbon electrode and the aromatic anion radicals act as outer-sphere reagents, whereas the mercury electrode and the iron(I), iron(0), and cobalt(I) porphyrins react in an inner-sphere manner.

In this connection, let us first discuss the electrochemical data at carbon electrodes and the homogeneous reduction by aromatic anion radicals and examine them to see if they provide evidence

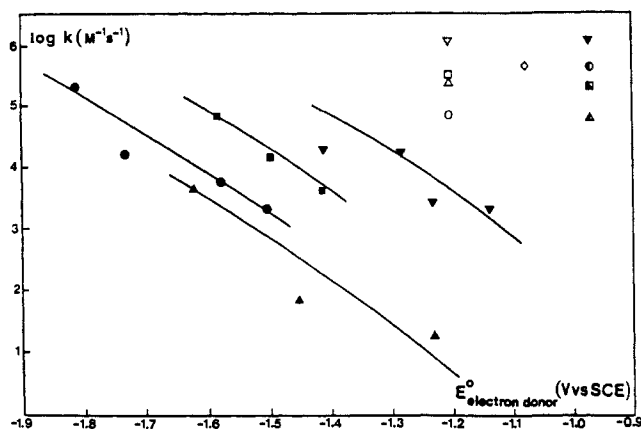


Figure 3. Reaction of electrogenerated anion radicals (solid symbols), OEPFe^I (open symbols), and OEPCo^I (half-open symbols) with 2,3-dibromo-2,3-dimethylbutane (▼, ▽, ▾), 1,2-dibromo-2-ethylbutane (■, □, ▣), 1,2-dibromooctane (●, ○, ◐), and 1,2-dibromoethane (▲, △, Δ). (◇) represents the reaction of 1,2-dibromoethane with e-(diC₄Ph)₂-CT-TPPFe^I. Variation of the rate constant with the standard potential of the electron donor. For the identification of each aromatic anion radical see Table II.

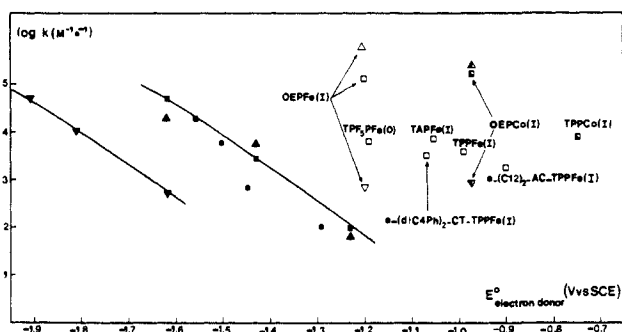
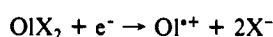


Figure 4. Reaction of electrogenerated anion radicals (solid symbols), iron(I) and iron(0) porphyrins (open symbols), and cobalt(I) porphyrins (half-open symbols) with *trans*-1,2-dibromocyclohexane (■, □, ▣), axial, axial-*trans*-1,2-dibromo-3-methylcyclohexane (▲, △, Δ), equatorial, equatorial-*trans*-1,2-dibromo-3-methylcyclohexane (▼, ▽, ▾). Variation of the rate constant with the standard potential of the electron donor. For the identification of each aromatic anion radical see Table III.

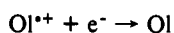
for the outer-sphere concerted single electron transfer bond-breaking mechanism (ET) sketched in the introduction rather than for other possible mechanisms.

In the framework of a one-electron per molecule rate-determining step, we first note that the values found from the transfer coefficient (Table I), ranging from 0.31 to 0.38, i.e., significantly smaller than 0.5, are a clear indication that the reaction does not proceed through the intermediacy of the dibromide anion radical akin to the case of alkyl monohalides.²⁵ This falls in line with the fact that no such anion radical appears in low-temperature ESR investigations of γ -ray irradiated vicinal dibromoalkanes.²⁶ In other words, the rate-determining step does not proceed in an outer-sphere manner from the point of view of both the electron donor and the dibromide. The electron donor may react in an outer-sphere manner but not the dibromide for which bond breaking of one or the two carbon-bromine bonds is concerted with electron transfer.

Besides the mechanism denoted "ET", two other conceivable mechanisms belong to the above category. Breaking of the second carbon-bromine bond may be concerted with electron transfer and with the breaking of the first carbon-bromine bond directly yielding the cation radical of the final olefin:

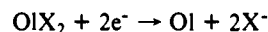


followed by:



One may also envisage that the breaking of the two carbon-

bromine bonds and the transfer of the two electrons might be concerted:



In order to examine whether or not these two mechanisms are compatible with the experimental data, we need an estimation of the standard potential, E° , of the latter reaction, which, although not the rate-determining step, represents the overall process. This can be obtained from existing gas-phase thermochemical data, assuming that the free enthalpies of solvation of OIX₂ and OI are not too different.²⁷ The values of E° thus obtained are listed in Table I (fifth column).

On the other hand, the standard potential for the first electron transfer, E°_1 , in the case where it is rate-determining and whether it involves the cleavage of one or of the two carbon-bromine bonds, can be derived from the experimental data, i.e., from the values of E_m and α_m , by use of the following relationships:^{12a}

$$\Delta G_{0,\text{el}}^* = \frac{1}{4\alpha_m^2} \frac{RT}{F} \ln \left(\frac{Z^{\text{el}}}{k_m} \right) \quad (1)$$

$$E^\circ_1 = E_m + \frac{4\Delta G_{0,\text{el}}^* (1 - 2\alpha_m)}{n} - \phi_r \quad (2)$$

with

$$\frac{RT}{F} \ln \left(\frac{Z^{\text{el}}}{k_m} \right) = \frac{RT}{F} \ln \left(\frac{Z^{\text{el}}}{(\alpha_m n \nu D F / RT)^{1/2}} \right) + 0.145 \frac{RT}{F} \quad (3)$$

which are based on a quadratic activation driving force relationship

$$\Delta G_{\text{el}}^* = \Delta G_{0,\text{el}}^* \left(1 + \frac{E_m - E^\circ_1 - \phi_r}{4\Delta G_{0,\text{el}}^*} \right)^2 \quad (4)$$

where

$$\alpha_m = 0.5 \left(1 + \frac{E_m - E^\circ_1 - \phi_r}{4\Delta G_{0,\text{el}}^*} \right) \quad (5)$$

and

$$k_m = Z^{\text{el}} \exp \left(- \frac{F\Delta G_{\text{el}}^*}{RT} \right) \quad (6)$$

$\Delta G_{0,\text{el}}^*$ is the standard activation free enthalpy for the electrochemical reaction (i.e., the activation free enthalpy at zero driving force or, equivalently, intrinsic barrier free enthalpy), and k_m is

(25) (a) A small value of the transfer coefficient indicates, in the framework of a quadratic activation driving force relationship, that the reduction potential is far from the standard potential of the rate-determining step, i.e., that the driving force is large. Since, as in the case of monohalides, the standard potential of the anion radical is close or negative to the reduction potential, it follows that the rate-determining step is the concerted process.^{25b} (b) Andrieux, C. P.; Gélis, L.; Médebielle, M.; Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* In press.

(26) (a) Symons, M. C. R. *Pure Appl. Chem.* 1981, 53, 223. (b) Maj, S. P.; Symons, M. C. R.; Trousson, P. M. R. *J. Chem. Soc., Chem. Commun.* 1984, 561. (c) See also the results of previous photochemical investigations.^{26d-e} (d) Shea, K. J.; Skell, P. S. *J. Am. Chem. Soc.* 1973, 95, 283. (e) Skell, P. S.; Pavlis, R. R.; Lewis, D. C.; Shea, K. J. *J. Am. Chem. Soc.* 1973, 95, 6735. (f) Shea, K. J.; Lewis, D. C.; Skell, P. S. *J. Am. Chem. Soc.* 1973, 95, 7768.

(27) (a) Benson, S. W. *Thermodynamical Kinetics*, 2nd ed.; Wiley: New York, 1976. (b) In a solvent such as DMF, which possesses a Brønsted basicity, dibromoalkanes being Brønsted acids should be more strongly solvated than olefins which are Brønsted bases. If different from the gas-phase values, the actual E° should thus be more negative. (c) In this estimation, we also neglected the small difference in the free energies of formation of the *E* and *Z* olefins that are obtained upon reduction of *erythro* (*meso*) and *threo* (*dl*) isomers. This is of no importance in the present qualitative discussion of the reduction mechanism but will be taken into consideration later on in the quantitative discussion of the stereospecificity in the reduction of **6** and **7**.

the value of the potential dependent heterogeneous rate constant at the potential E_m .²⁸ As noted earlier, the accuracy on α_m is rather poor so that its variations in the investigated dibromoalkane series cannot be considered as really meaningful. We thus treated the experimental data by means of the above equations taking for all compounds an average value of 0.35 with a standard deviation of 0.025. The resulting estimation of E°_1 is consequently not very precise, viz., within ± 0.3 V. This is, however, sufficient for the present discussion. The values of E°_1 , thus estimated are listed in Table I (sixth column under the heading $E^{\circ}_{1, \text{pred}}$). Note that $\Delta G_{0, \text{el}}^{\ddagger}$ is estimated to have a value between 0.6 and 0.8 eV according to this treatment.

The standard potential of the second electron transfer can now be derived from E° and E°_1 since

$$E^{\circ} = \frac{E^{\circ}_1 + E^{\circ}_2}{2}$$

E°_2 features either the reduction of OIX^* to OI and X^- or that of OI^{*+} to OI . The values of E°_2 thus predicted are listed in Table I (seventh column under the heading $E^{\circ}_{2, \text{pred}}$). The standard potentials for the oxidation of aliphatic olefins into their cation radicals are not known in DMF. However a correlation between the standard potential of the oxidation of aromatic hydrocarbons in this solvent and their vertical ionization potentials, I , has recently been established:²⁹

$$E^{\circ}(\text{V vs SCE}) = 0.85I(\text{eV}) - 4.86$$

This relationship can be used for estimating the olefin oxidation standard potentials. The resulting values are listed in Table I between parentheses just below the $E^{\circ}_{2, \text{pred}}$ values (seventh column). The latter are clearly not positive enough to correspond to the OI/OI^{*+} couple, even taking into account the ± 0.3 V uncertainty mentioned above.³⁰

The same relationships can be used to predict from the experimental data the standard potential of the $\text{OIX}_2 + 2e^- \rightleftharpoons \text{OI} + 2\text{X}^-$ couple, E°_{pred} , if this reaction is the rate-determining step. Even taking into account the large uncertainty involved in this prediction, ± 0.6 V, the values thus obtained (Table I, eighth column) are far too positive compared to those of E° (Table I, fifth column).

We are thus led to conclude that reduction of the vicinal dibromoalkanes on a carbon electrode follows the mechanism denoted "ET", i.e., involves as the rate-determining step a concerted single electron transfer bond-breaking reaction leading to the OIX^* radical. This falls in line with the fact that this radical has been clearly identified and characterized in low-temperature ESR investigations of γ -ray irradiated vicinal dibromoalkanes,^{26b} pointing to its intermediacy in the outer-sphere one-electron reduction of these compounds.

In the framework of this mechanism, let us now examine more closely the characteristics of the rate-determining step and how they vary in the series as a function of electronic and steric factors. Three important facts are apparent upon inspection of the variations of the reduction potential E_m .

(1) The antiperiplanar preference of the reaction clearly appears upon comparison of the E_m values of the axial-axial and equatorial-equatorial conformers **14** and **15**.

(28) (a) Here, and throughout the paper, the potentials are expressed in volts and the energies in eV. (b) Z^{\ddagger} is the heterogeneous collision frequency that we take, from the Debye-Smoluchowski equation,^{28c} as being equal to $4 \times 10^5 \text{ cm}^{-1}$ on the average in the whole dibromoalkane series. (c) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265. (d) Φ_s is the potential difference between the reaction site and the solution. In the framework of the Frumkin procedure for correcting the effect of the double layer on charge-transfer kinetics, the reaction site is assumed to be located in the outer Helmholtz plane.^{28e} Φ_s data are not available for a glassy carbon electrode in DMF with a tetraalkylammonium salt as the supporting electrolyte. We, however, know from available data for the mercury electrode that this term is small, on the order of -0.1 V.^{28f} It will be thus neglected in the following. (e) Delahay, P. *Double Layer and Electrode Kinetics*; Interscience: New York, 1965; pp 153-167. (f) Fawcett, W. R.; Ikeda, B. M.; Sellan, J. B. *Can. J. Chem.* **1979**, *57*, 2268. (g) D is the diffusion coefficient of the dibromide, for which we took an average value of $9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

(29) Anxolabéhère, E.; Hapiot, P.; Savéant, J. M. *J. Electroanal. Chem.* **1990**, *282*, 275.

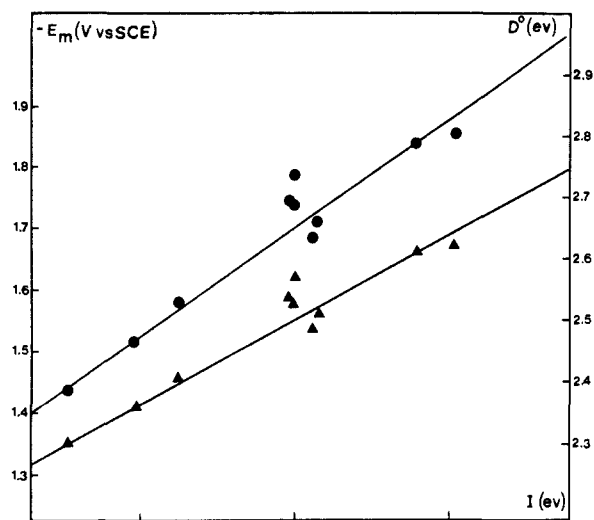


Figure 5. Correlation of the reduction potential, E_m (●), at 0.1 V s^{-1} and the bond dissociation energy of OIX_2 , D° , (▲) with the ionization potential of the olefin, I .

torial-equatorial conformers **14** and **15**. (2) *trans*-1,2-Dibromocyclohexane (**16**) has a reduction potential very close to that of the axial-axial conformer **14**. (3) Substitution at carbon makes the reduction potential increasingly more positive. In this connection, there is a striking parallelism between the variations of E_m and those of the ionization potentials^{30b} in the acyclic series (Figure 5).

In the framework of the ET mechanism, these effects imply that the stability of OIX^* , or more precisely the dissociation energy of the C-X bond in OIX_2 ($\rightarrow \text{OIX}^* + \text{X}^*$), D° , varies accordingly. D° is indeed the main factor of the variation of the standard potential E°_1 (the larger D° , the more negative the standard potential) and of the intrinsic barrier, $\Delta G_{0, \text{el}}^{\ddagger}$ (the larger D° , the higher the intrinsic barrier^{9c,d}). OIX^* would thus be stabilized as a consequence of the antiperiplanar arrangement of the starting compound and by increased substitution at the functional carbons. This can be rationalized as follows. The ESR spectra of β -bromoalkyl radicals reveal a strong coupling between the unpaired electron and the bromine atom.²⁶ In other words, in the absence of steric constraints, the C-C and C-X bond possess a partial double bond character owing to the coupling of the p_z orbital containing the unpaired electron with the C-X σ^* orbital.³¹ The situation is thus similar to that of the β -halocarbanion intermediate of β -elimination reactions where the sp^3 orbital containing the electron pair couples with the C-X σ^* orbital.^{31b}

The antiperiplanar preference of the reaction is thus a consequence of the angle between the p_z orbital and the C-X bond being more favorable in the a-a (**14**) than in the e-e (**15**) conformer (In the starting compound, the angle between the two C-X bonds is close to 180° in the a-a conformer and close to 70° in the e-e conformer. In OIX^* , the angle between the p_z orbital containing the unpaired electron and the C-X bond should have approximately the same values.).

Delocalization of the unpaired electrons will also be enhanced by carbon substitution similarly to what has been previously observed in the case of the β -halocarbanion intermediate of β -elimination reactions.³² In other words, the resonance form

(30) (a) Taking into account that E° may be somewhat more negative than the values listed in Table I,^{27b} the same would be true for E°_2 thus reinforcing the present conclusion. (b) The vertical ionization potentials were obtained from ref 30c-f. (c) Kiser, R. W. *Introduction to Mass Spectrometry and its Applications*; Prentice Hall: Englewood Cliffs, NJ, 1965; p 308. (d) Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* **1969**, *50*, 664. (e) Franklin et al. *Ionization Potentials, Appearance Potentials and Heat of Formation of Gaseous Positive Ions*; U.S. Department of Commerce, 1969. (f) Masclet, P.; Grojean, D.; Mouvier, G.; Dubois, J. *J. Electron Spectrosc.* **1973**, *2*, 225.

(31) (a) Note that the OIX^* radical does not appear to be bridged through the bromine atom. Rather, the bromine atom exchanges rapidly between the two functional carbons.²⁶ (b) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 177, 178.

*C-C*X* is stabilized by increased substitution at carbon. This resonance form bears some resemblance with the cation radical of the olefin. However, the halide ion has been expelled in the latter case as opposed to the former. This falls in line with the fact that E_m is linearly correlated with the ionization potential and also with the fact that the slope of the correlation (0.35) is small (Figure 5), confirming that the intermediate product of the rate-determining step is not the cation radical of the olefin.

The antiperiplanar preference of the reaction also allows one to understand why the reduction of *trans*-1,2-dibromocyclohexane on glassy carbon exhibits almost the same characteristics as the axial-axial conformer **14**. *trans*-1,2-Dibromocyclohexane exists as a 34:66 mixture of the axial-axial and equatorial-equatorial isomers in DMF.^{33a} As the former is reduced at the electrode surface, the latter is rapidly converted into the former (at 20 °C), the isomerization reaction constantly remaining at equilibrium, in the framework of a "CE" mechanism.^{33b,c} In view of the equilibrium composition of the isomer mixture, E_m for the mixture is expected to be slightly more negative (by ca. 70 mV) than E_m for the *a-a* isomer, in agreement with what is found experimentally (40 mV).

In the acyclic series, we can likewise consider that the anti conformers are easier to reduce than the gauche conformers and thus that the reduction of the whole mixture goes through the anti conformer, the conversion reaction remaining constantly at equilibrium.

The slight differences in E_m we find between **6** and **7** (100 mV) and between **8** and **9** (50 mV) result in this framework from the different proportions of anti vs gauche conformers in the *meso* (*erythro*) isomer as compared to the *dl* (*threo*) isomer and from the different stabilities of the anti conformers in the two isomers. The same should be true at the preparative scale electrolysis provided "mild conditions"^{12c} are used, i.e., the electrolysis potential is not very negative to the reduction potential as it appears in slow scan cyclic voltammetry.

These small potential shifts were neglected in the preceding qualitative discussion of the reduction mechanism. We continue to neglect them to a first approximation (they will be analyzed in more detail in the following with the examples of **6** and **7**) and examine, in a more quantitative manner, how the stability of OIX*, or equivalently the bond dissociation energy, influences the reduction potential, E_m , through its relationships with the standard potential, E°_1 , and the intrinsic barrier, $\Delta G^\ddagger_{0,el}$.

E°_1 is related to D° as follows

$$E^\circ_1 = \mu^\circ[\text{OIX}_2] - \mu^\circ[\text{OIX}^*] - \mu^\circ[\text{X}^-] = -D^\circ - T[s(\text{OIX}_2) - s(\text{OIX}^*) - s(\text{X}^-)] + E^\circ[\text{X}^*/\text{X}^-]$$

where μ° and the s are the standard chemical potentials (in eV) and the partial molar entropies respectively. The last terms vary by less than ± 0.03 eV in the series.^{27a} It follows that

$$E^\circ_1(\text{V vs SCE}) = -D^\circ (\text{eV}) + 1.82 \quad (7)$$

On the other hand, the contribution of bond breaking to the standard activation energy can be related to the bond energy of the C-X bond as in the case of the similar concerted electron-transfer bond-breaking reaction to alkyl monohalides, i.e., estimated as equal to one fourth of the bond energy.^{9c,d} The contribution of solvent reorganization is much smaller^{9c} and can be estimated as equal to 0.13 eV on average as discussed earlier.^{12a} Thus

$$\Delta G^\ddagger_0 = \frac{D^\circ}{4} + 0.13 (\text{in eV}) \quad (8)$$

Manipulation of eqs 1-5 leads to

(32) (a) Biale, G.; Cook, D.; Loyd, D. J.; Parker, A. J.; Stevens, I. B. R.; Takahashi, J.; Winstein, S. *J. Am. Chem. Soc.* **1971**, *93*, 4735. (b) Beltrame, P.; Biale, G.; Loyd, D. J.; Parker, A. J.; Ruane, M.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2240.

(33) (a) Abraham, R. J.; Rossetti, Z. L. *J. Chem. Soc., Perkin Trans. 2* **1973**, 582. (b) Savèant, J. M.; Vianello, E. *Electrochim. Acta* **1963**, *8*, 905. (c) This point has been fully established by a careful study of the temperature dependence of the cyclic voltammetry of *trans*-1,2-dibromocyclohexane in *n*-butyronitrile.^{15b,c}

$$D^\circ = \frac{1}{2} \left\{ \left[E_m - 1.3 - \frac{RT}{F} \ln \left(\frac{Z_{el}}{k_m} \right) \right] + \Delta^{1/2} \right\} \quad (9)$$

with

$$\Delta = \left[E_m - 1.3 - \frac{RT}{F} \ln \left(\frac{Z_{el}}{k_m} \right) \right]^2 - \left[(E_m - 1.3)^2 - 2.08 \frac{RT}{F} \ln \left(\frac{Z_{el}}{k_m} \right) \right] \quad (10)$$

which allows the estimation of D° from the experimental data, viz., E_m and $(RT/F) \ln (Z_{el}/k_m)$. We note that the latter quantity varies very little (from 0.355 to 0.358) in the whole series showing that the effect of the inaccuracy of a_m determination on the calculation through eq 3 is very small. The values of D° , thus estimated, are listed in Table I under the heading D°_{el} (tenth column) which recalls that they are derived from electrochemical data. On this basis, i.e., in the framework of the dissociative electron-transfer model^{9c,d} that we have been applying so far, it is also possible to estimate the standard activation free energy, ΔG^\ddagger_0 , from eq 8 and thus, also, α_m from eq 1 and to compare the values of α_m thus estimated to the experimental values. This could look, at first sight, like a circular argument since the experimental values of α_m were used, at the start of the calculation, to obtain $(RT/F) \ln (Z_{el}/k_m)$ by means of eq 3 and then to obtain α_m by means of eqs 8-10. It is in fact not the case since the experimental value of α_m is used at the start of the calculation merely as the initial guessed value of an iteration procedure. If the latter is pursued, it converges quite rapidly, so rapidly that the first and final values of D° and ΔG^\ddagger_0 (and for α_m the second and final values) are practically the same. The values of ΔG^\ddagger_0 and α_m thus obtained are listed in Table I under the headings $\Delta G^\ddagger_{0,el}$ and α_m^{th} , respectively (11th and 12th columns).

There is a good agreement between the theoretical and experimental values of α_m , showing that the dissociative electron transfer model^{9c,d} provides a satisfactory description of the kinetics of the rate-determining step in the ET mechanism.

A test of the self-consistency of the above data processing is provided by the comparison between the values of E°_1 previously estimated ($E^\circ_{1,pred}$) and those that can be derived from the D° values by means of eq 4 ($E^\circ_{1,th}$). It is seen that these two series of values are in good agreement within the range of uncertainty previously established for $E^\circ_{1,pred}$.

Let us now examine the kinetics of the homogeneous reaction of dibromoalkanes with the electrogenerated aromatic anion radicals. It is immediately seen that they follow the same trends as for the carbon electrode electrochemical data (Figures 3 and 4): antiperiplanar preference (at the same standard potential of the electron donor, the reaction is faster, by a factor of ca. 100 with **14** than with **15**; **14**, and **16** react at about the same rate), acceleration of the reaction by alkyl substitution at the functional carbons. A quantitative analysis of the kinetic data can be carried out along the same lines as for the electrochemical data in the context of a concerted electron-transfer bond-breaking mechanism. The activation free energy, ΔG^\ddagger_{hom} , is related to the standard activation energy $\Delta G^\ddagger_{0,hom}$ and the driving force of the reaction, $E^\circ_{ed} - E^\circ_1$ (E°_{ed} : standard potential of the electron donor), by a quadratic relationship^{9c,d}

$$\Delta G^\ddagger_{hom} = \Delta G^\ddagger_{0,hom} \left(1 + \frac{E^\circ_{ed} - E^\circ_1}{4\Delta G^\ddagger_{0,hom}} \right)^2 \quad (11)$$

with

$$\Delta G^\ddagger_{0,hom} = \frac{D^\circ}{4} + 0.13 \quad (12)$$

(the last small term represents the solvent reorganization free energy)

$$\frac{RT}{F} \ln k = \frac{RT}{F} Z^{hom} - \Delta G^\ddagger_{hom} \quad (13)$$

(Z^{hom} : homogeneous collision frequency, equal to $4 \cdot 10^{11} \times \text{M}^{-1} \text{s}^{-1}$ on the average^{12a}). On the other hand, E°_1 is related to D° by eq 4. We can thus fit the experimental data by eq 11 and 13 (Figures 3 and 4) and thus derive a value of D° using eqs 7 and 12. The resulting values of D° (denoted D°_{hom} for indicating that they come from experimental homogeneous kinetic data) are listed in Table I (14th column). It is seen that they are in excellent agreement with the values obtained from the direct electrochemical reduction at a carbon electrode.

It is interesting to compare the values of D° we just obtained to those that can be estimated from known thermochemical data, D°_{est} , assuming the validity of the additivity rule^{27a} for the heat of formation of the OIX* radical

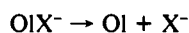
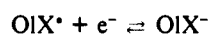
$$F(\text{OIX}^*) = F(\text{OIH}^*) - F(\text{C-H}) + F(\text{C-X})$$

i.e., ignoring the possible stabilization of OIX* by the presence of the remaining bromine atom. The values of D°_{est} thus obtained are listed in Table I (ninth column). It is seen that they are comprised between 2.8 and 3.0 eV, i.e., close, as expected, to the values estimated in the same way for alkyl monobromides.^{3c} The difference between D°_{est} and D°_{el} (the values of which are listed between parentheses in the 10th column of table I) is thus a gross estimate of the stabilization of the OIX* radical as a result of the delocalization of the unpaired electron. This ranges from 0.23 to 0.41 eV in the series except for compound 15. It is remarkable that 15, in which the C*p_z and C-Br σ^* orbitals practically do not interact, also exhibits a very small difference between D°_{el} and D°_{est} . This compound could serve as a reference for estimating the stabilization of OIX* in the rest of the series, in which case the stabilization free energies would range from 0.14 to 0.32 eV.

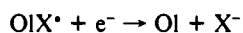
At this stage we can thus conclude that the electrochemical reduction at an inert electrode (such as carbon) as well as by homogeneous outer-sphere reagents (such as aromatic anion radicals) of vic-dibromoalkanes proceeds along a concerted single electron transfer bond-breaking rate-determining step leading to the β -bromoalkyl radical. The latter is stabilized by delocalization of the unpaired electron over the C-C-Br framework.

How the β -bromoalkyl radical is reduced into the final olefin is worth some comment. Four mechanisms are conceivable for this reaction:

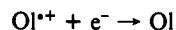
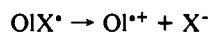
stepwise electron transfer and cleavage of the halide ion



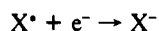
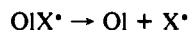
concerted electron transfer and cleavage of the halide ion



stepwise cleavage of the halide ion and electron transfer

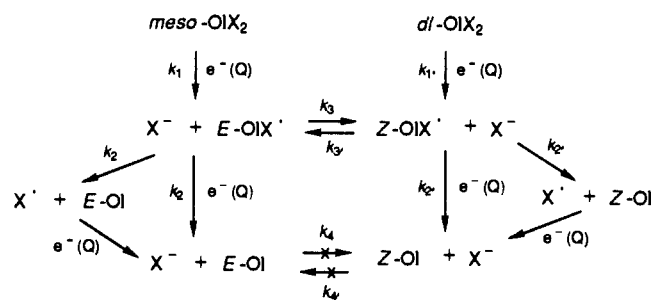


stepwise cleavage of the halogen atom and electron transfer



All these reaction pathways have, of course, the same thermodynamics, characterized by the standard potential E°_2 . With regard to the second of them, an estimate of the dissociation energy of the C-X bond in the OIX* radical can be obtained from eq 7, relating the bond dissociation energy to the standard potential of the concerted electron-transfer bond-breaking reaction that has been already used for the conversion of OIX₂ into OIX*. E°_2 , which now replaces E°_1 in the equation, is of the order of 1 V vs SCE. $D^{\circ}_{\text{OIX}^*}$ is thus of the order of 0.9 eV. This quite small value, as compared to the dissociation of OIX₂ into OIX*, results from the strong driving force offered by the formation of the double bond. Thus, if we apply the same kinetic model for this concerted electron-transfer bond-breaking reaction as we have applied for the OIX₂ + e⁻ → OIX* + X⁻ reaction,^{9c,d} we predict

Scheme 1



an intrinsic barrier, ΔG_0^\ddagger , on the order of 0.36 eV (0.23 for bond breaking and 0.13 for solvent reorganization). In the first reaction pathway, the second step having a large driving force is certainly very rapid and thus the rate-determining step is the first electron transfer. In view of the large driving force for the second step, the standard potential of the electron transfer is much less positive than E°_2 , probably somewhat cathodic to zero by reference to the E° s of alkyl (-1.4 V vs SCE)³⁴ and perfluoroalkyl (-0.5 V vs SCE)^{25b} radicals. Electron transfer to these radicals has been shown to possess a rather large intrinsic barrier due to both solvent reorientation and geometrical changes.^{34,25b} The same is most probably true in the present case. Thus, the conversion of OIX* into OIX⁻ has both a considerably more negative standard potential and a larger intrinsic barrier than the concerted electron-transfer bond-breaking pathway. The latter has such a positive standard potential and such a small intrinsic barrier that, at the potential where it is generated from OIX₂, it should be in the "inverted region" if one would assume that a quadratic activation driving force relationship (eq 4) still holds at such large driving forces. In fact, an almost barrierless process is more likely.³⁵ For these reasons the second pathway should predominate over the first both in the direct and mediated electrochemical reductions of OIX₂. In the latter case the reaction will in fact be under diffusion control. In the third pathway, the first step has a very poor driving force since the standard potential of the OI^{*+}/OI couple is much more positive than E°_2 (Table I, seventh column). It is thus unlikely to compete with the second pathway. The fourth mechanism is a conceivable alternative to the second in the case of a homogeneous reduction if the expulsion of the bromine atom is so rapid as to occur within the solvent cage and thus to compete with the diffusion-controlled concerted electron-transfer bond-breaking pathway. The rate constant of bromine expulsion in similar β -bromoalkyl radicals has been determined to be 10^8 s^{-1} in benzene.^{36a} No large solvent effects are anticipated for such a reaction, and this figure can thus be taken as an estimation of the rate constant of the reaction in our case. The competition between the second and fourth pathways will thus be in favor of the latter as soon as the effective concentration of the aromatic anion radical in the reaction layer is smaller than 20 mM.^{36b} This

(34) Andrieux, C. P.; Gallardo, I.; Savéant, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 1620.

(35) (a) Although the "inverted region" has been detected in several instances for purely outer-sphere processes,^{35b-k} nuclear tunneling is known to counteract this behavior. This is even more likely in the case of a concerted electron-transfer bond-breaking pathway. (b) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1986**, *106*, 5057. (c) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (d) Snadrini, D.; Maestri, M.; Belsler, P.; von Zelewsky, A.; Balzani, V. *J. Phys. Chem.* **1985**, *89*, 3075. (e) Wasielewski, M. R.; Niemczyk, M. R.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080. (f) Gunner, M. R.; Robertson, D. E.; Dutton, P. L. *J. Phys. Chem.* **1986**, *90*, 3783. (g) Ohno, T.; Yoshimura, A.; Mataga, N. *J. Phys. Chem.* **1986**, *90*, 3295. (h) Ohno, T.; Yoshimura, A.; Shioyama, H.; Mataga, N. *J. Phys. Chem.* **1987**, *91*, 4365. (i) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *83*, 3675. (j) McLendon, G. *Acc. Chem. Res.* **1988**, *21*, 160. (k) Fox, L. S.; Gray, H. B. *Science* **1990**, *247*, 1069.

(36) (a) Wagner, P. J.; Sedon, J. H.; Linstrom, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 2579. (b) In DMF, $k_{\text{diff}} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Since the electrolysis potential is approximately located at the standard potential of the mediator, the concentration of Q at the electrode surface is half of its bulk concentration, and the average concentration in the reaction layer is half the concentration at the electrode.

is the case in the homogeneous catalysis cyclic voltammetry experiments and also in the preparative scale electrolyses described in Table IV. In the heterogeneous reduction the second (barrierless) pathway is likely to prevail over the fourth, because the OIX[•] radical is produced at the electrode surface and will thus be reduced there before having time to diffuse away and decompose into OI and X[•].

Let us now discuss the results of the stereoselectivity experiments (Table IV). In the case of the reduction by an aromatic anion radical, so far deemed on kinetic grounds to function as an outer-sphere reagent, partial stereospecificity is observed. Complete stereospecificity would imply to obtain from *meso*-OIX₂ an *E:Z* ratio of 100:0 and from *dl*-OIX₂ an *E:Z* ratio of 0:100; total absence of stereospecificity would lead to the same *E:Z* ratio in both cases. A ratio of 87:13 is obtained with *meso*-OIX₂ and of 38:62 with *dl*-OIX₂. This partial loss of the stereoselectivity results from the competition between rotation around the C–C bond in the OIX[•] radical and either its diffusion-controlled reduction by an aromatic anion radical molecule or its decomposition into OI and X[•] (Scheme I).

The rotation around the C–C bond is opposed by its partial double bond character deriving from the delocalization of the unpaired electron over the C–C–Br framework as discussed earlier. In other words, the OIX[•] radical exists in two stable forms having both a periplanar conformation, an *E*-like form, and a *Z*-like that interconvert more rapidly than the *E* and *Z* olefins but more slowly than rotation around a σ bond. In these two forms, the double bond character is approximately the same. The difference of stabilities between the two thus derives from the interactions between the groups attached to each carbon at the C–C bond. These should not be too different from what they are in the *E*- and *Z*-olefins. We can therefore assume that the equilibrium constants K_3 and K_4 are approximately equal. Another consequence of these approximations is that the standard potential, E°_2 , of the OIX[•] + e[−] ⇌ OI + X[•] reaction is the same for the *E*- and *Z*-forms. Application of the steady-state assumption to the two forms of the OIX[•] radical leads to the following equation that relates the ratio of the yields in *E*- and *Z*-olefins to the rate constants of the various steps

$$\frac{E}{Z}(\textit{meso}) = \frac{k_2(k_2' + k_3)}{k_2k_3}, \quad \frac{E}{Z}(\textit{dl}) = \frac{k_2k_3'}{k_2(k_2 + k_3)} \quad (14)$$

Since both reactions 2 and 2' are at the diffusion limit

$$k_2 = k_2' = k_{\text{dif}}[Q]$$

where $[Q]$ is the average concentration of the reduced form of the mediator in the reaction layer adjacent to the reaction surface where all reactions, depicted in the above scheme, take place. Equations 14 thus simplify into

$$\frac{E}{Z}(\textit{meso}) = \frac{k_3' + k_{\text{dif}}[Q]}{k_3}, \quad \frac{E}{Z}(\textit{dl}) = \frac{k_3}{k_3 + k_{\text{dif}}[Q]} \quad (15)$$

On the other hand, k_3 and k_3' can be expressed as

$$k_3 = k_3^0(k_3)^{1/2}, \quad k_3' = k_3^0(k_3)^{-1/2} \quad (16)$$

with

$$k_3^0 = A \exp\left(-F \frac{\Delta G_3}{RT}\right) \quad (17)$$

in which k_3^0 is a "standard rate constant for the rotation around the C–C bond", i.e., the common value of the rate constants that reactions 3 and 3' would have if the *E*- and *Z*-forms of the OIX[•] radical had the same free energy. k_3^0 is related through eq 17 to the free energy representing the amount of double bond character³⁷ of the C–C bond in the OIX[•] radical, i.e., the stabilization energy that we have discussed and approximately estimated before. k_3 and k_3' are related to k_3^0 through eq 16 in which it is assumed that the driving force of the reaction, represented by its equilibrium constant K_3 , shares its effect on the kinetics in two halves, one for accelerating the forward reaction and the other for decelerating the backward reaction.^{37c} Combining eqs 15–17, estimates of

Table IV. Yields of (*E*)- and (*Z*)-4-Octenes upon Direct and Mediated Electrolysis of *meso*-(6) and *dl*-4,5-Dibromooctanes (7)^a

Direct Electrolyses				
4,5-dibromooctane	cathode		4-octene/ 4-bromo- 4-octene	<i>E:Z</i>
	material	potential ^b		
6	GC	−1.78	82:18	100:0
	GC	−1.82	85:15	100:0
7	Hg	−1.92	55:44	10:90 ^c
6	Hg	−1.56	91:9	100:0
7	Hg	−1.68	93:7	1:99
Indirect Electrolyses				
4,5-dibromooctane	mediator (concn in mM)	cathode potential ^b	4-octene/ 4-bromo- 4-octene	<i>E:Z</i>
6	1,4-diacetylbenzene (57)	−1.41	98:2	87:13
	(5.7)	−1.41	51:49	87:13
	7 (57)	−1.41	85:15	36:64
	(11.4)	−1.41	56:44	41:59
6	OEPPe (1.4)	−1.23	72:28	100:0
		−1.23	91:9	0:100
6	ETIOPCo (1.4)	−1.03	82:18	100:0
		−1.03	95:5	0:100

^a In DMF + 0.1 M Bu₄NBF₄. Dibromooctane concn. 57 mM unless otherwise stated. ^b In V vs SCE. ^c Average of three determinations.

Table V. Conformer Stabilities in *meso*- and *dl*-4,5-Dibromooctanes

4,5-dibromo-octane	BrC–CBr dihedral angle (deg)	con- former ^a	H ^f (Kcal/ mol)	fraction of A at equilibrium	E_m D ^o _{el} for the A conformer
<i>meso</i> -6	180	A	−51.57	0.31	−1.660,
	67	G1	−51.62		2.52
	−67	G2	−51.62		
<i>dl</i> -7	161	A	−53.17	0.87	−1.834,
	60	G1	−51.67		2.63
	−60	G2	−51.67		

^a A, antic conformer; G1, G2, gauche conformers.

K_3 and ΔG_3 can be derived from the experimental values of the *E:Z* ratio for the *meso*- and *dl*-4,5-dibromooctanes, taking $k_2 = k_2' = 10^8 \text{ s}^{-1}$. We thus find³⁷ $K_3 = 0.34$ and $\Delta G_3 = 0.31 \text{ eV}$. As seen earlier, $K_3 = K_4$. We thus predict an equilibrium *E:Z* ratio of 75:25 for 4-octene.

How does this compare with literature data? From gas-phase thermochemical data,^{27b} K_4 is found to be 0.14; more exactly taking the uncertainties on the energies and entropies of formation into account, K_4 is comprised between 0.02 and 1, i.e., the *E:Z* ratio is 88:12, in fact, comprised between 50:50 and 98:2. For a closely similar compound, viz., 3-hexene, the *E:Z* ratio is found to be 88:12 from gas-phase thermochemical data and 69:31 from solution data obtained in liquid ammonia at −40 °C.^{12c} The results obtained under conditions that are probably the closest to ours concern the reaction of *meso*- and *dl*-2,3-dichlorobutanes with alkali naphthalenes in dimethoxyethane at room temperature in which an *E:Z* ratio of 75:25 was obtained starting from either the *meso* or the *dl* isomer^{17c} and which can therefore be taken as the thermodynamic equilibrium ratio. The equilibrium distribution of the *E*- and *Z*-isomers indicated by the present experiments thus falls satisfactorily within the range of uncertainty of the data available from independent sources.

Let us see now if the value of ΔG_3 derived from the stereospecificity experiments is consistent with the stabilization energy

(37) (a) By analogy with what happens in true olefins.^{36b} (b) See pp 72–74 in ref 27a. (c) This assumes, as seems likely, that in the rotation around the C–C bond both forms of the OIX[•] radical behave as harmonic oscillators with the same force constant. (d) The preexponential factor, A , is close to 10^{13} s^{-1} .^{37b}

of the OIX^{*} radical previously derived from the analysis of the cyclic voltammetry data. To do this, we need to analyze the data pertaining to the *meso*- and *dl*-4,5-dibromooctanes in a more precise manner than done earlier for the whole series of dibromo compounds. Table V gives the enthalpies of formation of the various stable conformers as calculated from the MMX force field method,^{38a,b} an improvement of the Allinger MM2 force field method.^{38c} From these, the fraction of the anti conformer can be estimated for each isomer and hence the values of E_m characterizing the *meso* and *dl* anti conformers assuming, as discussed earlier, that equilibrium between the *gauche* and anti conformers is achieved at low scan rates at 20 °C and therefore that the reduction goes entirely through the most reducible anti conformer. Thus

$$E_m(\text{anti}) = E(\text{observed}) + \frac{RT}{\alpha_m F} \ln \frac{[A]}{[G_1 + G_2]} \quad (18)$$

Then the dissociation energy for each anti conformer, D_{el}^0 , is derived from eq 3, 9, and 10 and the results listed in Table V (last column). Since

$$D_{\text{el},7}^0 - D_{\text{el},6}^0 = H_{\text{OIX},6}^* - H_{\text{OIX},7}^* + H_{\text{OIX}^*,7} - H_{\text{OIX}^*,6} \quad (19)$$

it follows, using the values listed in Table V, that

$$H_{\text{OIX}^*,7} - H_{\text{OIX}^*,6} = 0.04 \text{ eV} \quad (20)$$

from which the *E:Z* ratio, at the level of the OIX^{*} radicals, can be estimated (neglecting the difference in the entropies of formation) as 82:18, in good accord with the value derived earlier from the stereospecificity experiments. This is a confirmation of the assumptions made in the analysis of these experiments. The enthalpy of formation of the OIX^{*} radical as derived from thermochemical data²⁷ has a value of -45.81 Kcal/mol. This can be taken as the absolute value for the enthalpy of formation of the anti conformer of *dl*-4,5-dibromooctane since the van der Waals interactions are minimal in this compound as compared to all the other conformers of the *dl* compound and of all conformers of the *meso* compound. In this framework, the enthalpy of formation of the anti conformer of the *meso*-dibromide would then be -44.21 Kcal/mol. Since the enthalpy of formation of the Br atom is 26.74 Kcal/mol,^{27a} the enthalpy of formation of the OIX^{*} radical would then be -12.90 and -11.97 kcal/mol for the *E*- and *Z*-forms, respectively. On the other hand, according to the same thermochemical data,^{27b} the enthalpy of formation of the OIX^{*} radical is -4.55 Kcal/mol on purely additive grounds, i.e., ignoring the partial double bond character of the C-C bond. It follows that the stabilization of the C-C bond by its partial double bond character is 0.36 and 0.32 eV for the *E*- and *Z*-form, respectively. Thus $\Delta G_s = 0.34$ eV, a value which is in quite good agreement with the value, 0.31, derived from the stereospecificity experiments. The accuracy of the thermochemical data used in the above estimation is on the order of 1-2 Kcal (0.04-0.06 eV). Another, more direct estimate of the stabilization energy in the OIX^{*} radical is the difference between the bond dissociation energies derived from the electrochemical (10th column in Table I) or homogeneous (14th column in Table I) data for the a-a and e-e conformers **14** and **15**. The value thus found is comprised between 0.22 and 0.29 and is again in good agreement with what is found from the stereoselectivity experiments.

Stereospecificity results previously obtained for the reduction of similar compounds, viz., 2,3-dibromo- and 2,3-dichlorobutanes,^{17c} also fall within the same mechanistic framework. Although the *E:Z* ratios obtained with the *meso*- and *dl*-2,3-dibromobutanes suffer from some scatter, the same analysis as above would predict a value of K_4 of ca. 0.4, to be compared with 0.33 as derived from the thermodynamic equilibrium data, and a value of ΔG_s around 0.28, i.e., very close to that found with the 4,5-dibromooctanes. The *meso*- and *dl*-dichlorobutanes give rise to

the same *E:Z* equilibrium ratio. This can be rationalized as follows. The rotation around the C-C bond is expected to be faster in OICl^{*} than in OIBr^{*}, because the delocalization of the unpaired electron over the C-C-X framework is likely to be less in the first case than in the second. On the other hand, the expulsion of the X atom is expected to be slower. It may well become slower than the concerted electron-transfer bond-breaking reduction by the aromatic anion radical which is likely to remain at the diffusion limit. In any case, the total loss of stereospecificity is essentially related to the faster rotation around the C-C bond of the β -haloalkyl radical.

In the electrochemical reduction of *meso*- and *dl*-3,4-dibromohexanes,^{12c} complete stereospecificity is reached under "mild" reducing conditions, i.e., not too negative electrolysis potential, whereas equilibration is observed at a very negative potential and also when using solvated electrons as the reductant. The "mild" conditions are the same as in the present work for both electrochemical and aromatic anion radical reduction. Then the reduction goes entirely through the most reducible conformer, namely the anti periplanar conformer leading to the stereochemistry described above. This condition is no longer fulfilled at very negative potentials and in the reduction by solvated electrons. Then both the anti and syn conformers are simultaneously reduced, leading to a different stereochemistry.

The heterogeneous reductions at glassy carbon are almost totally stereospecific (Table IV) much more than the homogeneous reductions by aromatic anion radicals. This derives from the fact that the OIX^{*} radical is formed at the electrode surface where it is reduced very rapidly along an almost barrierless process. Rotation around the C-C bond is thus practically a surface reaction^{40a} and competes with another very fast surface reduction. Insofar rotation is viewed as a surface reaction, the *E:Z* ratios obtained upon reduction of the *meso*- and *dl*-dibromides can be predicted by means of a simple transformation of eqs 15-17.^{40b} $k_{\text{diff}}[Q]$ is replaced by k_s , the heterogeneous reduction rate constant, and k_3 and k_3' are multiplied by the depth from the electrode surface occupied by a monolayer of OIX^{*} radicals. The latter factor can be estimated as ca. 9 Å (6 for the distance of the outer Helmholtz plane from the surface with a Bu₄N⁺ supporting cation and 3 for the equivalent radius of the OIX^{*} radical). We thus find the value of k_s compatible with the *E:Z* distribution is 200 cm/s, which seems reasonable for an almost barrierless process (the heterogeneous collision frequency is ca. 4000 cm/s).

Let us now examine the reaction of *vic*-dibromoalkanes with the low oxidation state iron and cobalt porphyrins. A first indication of their inner-sphere character is the fact that they are much faster, by a factor of 10³-10⁴ for the iron porphyrins and 10⁵-10⁶ for the cobalt porphyrins, than the aromatic anion radicals that would have the same standard potential (Tables II and III, Figures 3 and 4). The same effect as already found in the particular case of OEPFe^I and OEPCo^I in their reaction with *trans*-1,2-dibromocyclohexane^{12a} thus appears as general in an extended series of *vic*-dibromo compounds and of cobalt(I) and iron(I) porphyrins. Note that the same is also found with an iron("0") porphyrin (TPF₃P). We also note that the antiperiplanar preference is maintained, being even slightly larger (by a factor of 10³ instead of 10²) than with aromatic anion radicals. Alkyl substitution at functional carbons does not seem, however, to have a large effect.

Among the various conceivable inner-sphere mechanisms, we can rule out an S_N2 attack at carbon^{41a} followed by elimination of Fe^{III}X or Co^{III}X in the case of Fe(I)⁻ and Co(I)⁻ and of Fe^{II}X⁻ in the case of Fe("0"). This follows from the antiperiplanar preference which would imply strong steric hindrance by the second bromine atom in the transition state. It is confirmed by the fact that the sterically congested e-(diC₄Ph)₂-CT-TPPFe^I complex reacts at almost the same rate as the unencumbered TAPFe^I complex which has about the same standard potential. It is also confirmed by the observation that the activation entropies derived from the Arrhenius plots shown in Figure 2 are about the same for OEPFe^I (4 eu) for the perylene anion radical (-2 eu).^{30c,d} The same lack of influence of steric hindrance is also found with

(38) (a) Gajewski, J. J.; Gilbert, K. E. Serena Software. (b) The method provides relative rather than absolute values of the enthalpies of formation. (c) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

Table VI. Characteristic Standard Potentials,^a Bromide Ion Association Constants,^b and Driving Forces^c for the Reaction with *trans*-1,2-Dibromocyclohexane of Iron(I) and Cobalt(I) Porphyrins in 1,2-Dichloroethane^d

porphyrin	$E^\circ_{\text{II/I}}$	$E^\circ_{\text{III/II}}$	$E^\circ_{\text{IIIX/IIIX}}$	K_{IIIX}	K_{IIIIX}	DF(ET) ^e	DF(HA) ^{f,g}	DF(E2) ^{f,h}
OEPFe ⁱ	-1.275		-0.568			0.443	0.532 (0.09)	2.061 (1.618)
TAPFe ^j	-1.048		-0.317	56		0.295	0.390 (0.095)	1.717 (1.422)
TPPFe ^j	-1.010		-0.297	80		0.226	0.360 (0.134)	1.668 (1.442)
a-(C12) ₂ -AC-TPPFe ⁱ	-0.879		-0.226			0.136	0.354 (0.218)	1.573 (1.437)
OEPCo	-1.095	0.632		<0.5	4.3×10^9	0.345	≤ 0.327 (≤ 0.02)	1.290 (0.945)

^aIn V vs SCE. ^bIn M⁻¹. ^cIn eV calculated from $E^\circ_{\text{I,th}}$ and E° (see Table I). ^d+0.1 M Bu₄NPF₆ at 20 °C. ^eFrom DMF data (see text). ^fFrom dichloroethane data. ^gBetween parentheses: DF(HA) - DF(ET). ^hBetween parentheses: DF(E2) - (ET). ⁱApproximated by the values for e-(C12)₂-CT and a-(C12)₂-CT, respectively.^{43c} ^jFrom ref 43c.

1,2-dibromoethane (Table II, Figure 3),^{41b} for which both reacting carbons being primary an S_N2 pathway would have had a better opportunity to compete with the other mechanisms.

Two other possible mechanisms remain, namely halogen atom (HA) and halonium ion (E2) abstraction. Both of them are expected to be faster than ET, owing to stabilizing bonding interactions in the transition state and to exhibit antiperiplanar preference due to partial delocalization of the electron density created at the attacked carbon in the transition state over the C-C-Br framework. Both mechanisms are compatible with the fact that the activation entropies are about the same as with outer-sphere electron donors such as aromatic anion radicals. The bromine atom indeed bears three lone electron pairs located in two orthogonal 4p orbitals (perpendicular to the Br-C bond) and in one 4s orbital. Formation of a partial bond in the transition state thus does not require a precise geometrical orientation of the attacking reactant unlike the case of an S_N2 attack at a carbon center. No significant influence of steric hindrance at the electron donor is likewise expected for both HA and E2 mechanisms.

The fact that total stereospecificity is obtained with both iron(I) and cobalt(I) porphyrins (Table IV) demonstrates that the reaction follows an E2 mechanism rather than a HA mechanism. In the latter case indeed, a partial loss of stereospecificity should occur as with the aromatic anion radicals since the reaction goes through the same OIX^{*} intermediate, in which the rotation around the C-C bond is responsible for the loss of stereospecificity.⁴² Total stereospecificity also confirms that, in the framework of halonium abstraction, the reaction is of the E2 rather than of the E1 type. In the latter case, indeed, rotation around the C-C bond in OIX⁻ is anticipated.^{22e} The predominance of the E2 over the HA mechanism can be rationalized on the following grounds.

The driving forces of the rate-determining steps in the ET, HA, and E2 mechanisms in the case of Fe(I)⁻ and Co(I)⁻ can be expressed as

$$\text{DF(ET)} = E^\circ_1 - E^\circ_{\text{II/I}}$$

$$\text{DF(HA)} = E^\circ_1 - E^\circ_{\text{II/I}} + \frac{RT}{F} \ln K_{\text{HX}}$$

$$\text{DF(E2)} = 2E^\circ - E^\circ_{\text{II/I}} - E^\circ_{\text{IIIX/IIIX}} + \frac{RT}{F} \ln K_{\text{IIIX}} = 2E^\circ - E^\circ_{\text{II/I}} - E^\circ_{\text{III/II}} + \frac{RT}{F} \ln K_{\text{IIIIX}}$$

(K_{IIIX} and K_{IIIIX} are the association constants of Br⁻ with the two- and three-valent complex, respectively, the subscript in the E° indicates the corresponding redox couple). It seems, at first sight, that we should, for estimating the driving forces, take the values of the E° and of the association constants in DMF. This is certainly true for the thermodynamic quantities featuring the dihaloalkane and its reduction products and intermediates as well as $E^\circ_{\text{II/I}}$ in the ET case. In the HA and E2 cases, however, the thermodynamic quantities pertaining to the metalloporphyrins correspond, since we start with Fe(I) or Co(I) porphyrins that are not axially complexed by DMF,^{43a} to the formation of the IIX

or IIIIX porphyrins before they react with DMF as a possible axial ligand. In these cases, we thus took the values that are obtained in a noncomplexing solvent, viz., 1,2-dichloroethane.^{43a} The resulting driving forces are given in Table VI for the case of *trans*-1,2-dibromocyclohexane (the same trends appear with the other dibromoalkanes).

It is seen that in the case of cobalt porphyrins there is no driving force advantage of the HA mechanism over the ET mechanism. On the opposite, the E2 mechanism has a strong driving force advantage (of the order of 1 V) deriving from the very strong complexation of Co(III) by Br⁻. In the case of iron(I) porphyrins, the HA mechanism has only a slight driving force advantage (ca. 0.1 eV) over the ET mechanism, whereas the E2 mechanism possesses a strong advantage (ca. 1.5 eV).

In the case of iron("0") porphyrins

$$\text{DF(HA)} - \text{DF(ET)} = \frac{RT}{F} \ln K_{\text{IX}}$$

$$\text{DF(E2)} - \text{DF(ET)} = 2E^\circ - E^\circ_1 - E^\circ_{\text{II/I}} + \frac{RT}{F} \ln K_{\text{IIIX}}$$

the HA mechanism is unlikely since iron(I) porphyrins have no

(40) (a) Savéant, J. M. *J. Electroanal. Chem.* **1980**, *112*, 175; **1983**, *143*, 447. (b) The isomerization of OIX^{*} by rotation around the C-C bond can alternatively be viewed as a homogeneous reaction coupled with its diffusion out of the electrode surface (over a short distance). The resolution of this electrochemical kinetic problem^{40c} leads to

$$\frac{E}{Z}(\text{meso}) = \frac{(1 + K_3)k_4 + [D(k_3 + k_3)]^{1/2}}{[D(k_3 + k_3)]^{1/2}}, \quad \frac{E}{Z}(dl) = \frac{K_3[D(k_3 + k_3)]^{1/2}}{(1 + K_3)k_4 + K_3[D(k_3 + k_3)]^{1/2}}$$

(D is the diffusion coefficient, assumed to be the same for all intervening species) the application of which leads to similar results as the surface reaction approach. (c) Savéant, J. M. Unpublished results.

(41) (a) This is the mechanism for the reaction of reduced iron and cobalt porphyrins with primary alkyl monobromides.^{5a,b} (b) At striking variance with what happens with *n*-butyl bromide and iron("0") porphyrins where the point corresponding to the sterically congested porphyrins falls on the outer-sphere reagent line, i.e., much below that of the unencumbered porphyrin. (c) The activation energies as derived from the slopes of the Arrhenius plots are 9.4 and 8.3 Kcal mol⁻¹, respectively. The activation entropies were derived from the Arrhenius plots taking as collision frequency 3×10^{11} M⁻¹ s⁻¹. (d) This is unlike what was found in the reaction of *n*-butyl bromide with iron("0") porphyrins and aromatic anion radicals. The activation entropy is ca. 15 eu smaller in the first case than in the second showing a carbon S_N2 attack as opposed to a concerted electron-transfer bond-breaking reduction, respectively.^{5b}

(42) In view of the differences between the standard potentials of the porphyrins and the reduction potential of OIX₂, the reduction of the OIX^{*} radicals is expected to be diffusion-controlled as in the case of aromatic anion radicals.

(43) (a) This procedure may underestimate the reactivity of Fe(I) and Co(I) since the more acidic (in the Brønsted sense) dichloroethane is likely to solvate them more than DMF. Furthermore, there might be a somewhat different junction potential between dichloroethane and DMF on one hand and the SCE reference electrode on the other. However, we can see that these effects are either small or compensate each other since the basket-handle iron porphyrins, a-(C12)₂-CT-TPP, have practically the same Fe(II)/Fe(I) standard potential in the two solvents. As discussed in detail elsewhere,^{42b} this couple can serve as a reference couple since Fe(I) is then poorly solvated by both solvents and Fe(II) poorly coordinated by DMF. (b) Gueutin, C.; Lexa, D.; Momenteau, M.; Savéant, J. M.; Xu, F. *Inorg. Chem.* **1986**, *25*, 4294. (c) Lexa, D.; Savéant, J. M.; Xu, F.; Momenteau, M. *J. Electroanal. Chem.* **1987**, *237*, 131.

(39) (a) The same has been invoked to explain a loss of stereoselectivity upon passing from I to Cl in different reactions likewise involving β-haloalkyl radicals.^{39b} (b) Russel, G. A.; Ngoviwathai, P.; Tashtoush, N. I.; Pla-Dalman, A.; Khanna, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 3530.

affinity for axial ligands. $2E^\circ - E^\circ_1 = 1.000$ V in the case of *trans*-1,2-dibromocyclohexane and $E^\circ_{11/1} = -0.789$ V vs SCE in the case of the Fe("0")²⁻ porphyrin we have investigated, viz. TPF₅P. There is thus a driving force advantage for the E2 mechanism even if the association of Br⁻ with the iron(II) porphyrin is a strong uphill process. This is true in general for the reaction of iron("0") porphyrins. With TPP, $K_{11X} = 80$. It is certainly larger for TPF₅P owing to the electron-withdrawing effects of the fluorosubstituents on the phenyl rings, leading to a driving force advantage of at least 1.9 eV.

The fact that aromatic anion radicals react with *vic*-dibromoalkanes in an outer-sphere fashion unlike iron(I), iron(0), and cobalt(I) porphyrins derives from their lack of halogen and halonium abstraction reactivity. This appears also to be the case for carbanions as exemplified by the fact that the rate constant for the reaction of the anion of dihydro-4-methoxycarbonyl-1-methylpyridine with 1,2-dichloro-1,2-diphenylethane falls on the same line as aromatic anion radicals^{14a,b} pointing to the conclusion that they react as outer-sphere electron-transfer agents. The driving force advantage of halonium abstraction over ET for an electron-donating X abstractor, D⁻, leading to DX, can be expressed as

$$DF(E2) - DF(ET) = E^\circ_2 - E^\circ_{DX/D_{\cdot+}X^-} \quad (21)$$

The values of the second standard potential for aliphatic carbanions and X = Br are on the order of -1 V vs SCE.^{9a,c} They can be much less negative for phenylmethyl carbanions, for example, 0.25 V vs SCE for 9-chloro-9-mesitylfluorene.⁴⁴ However, since E°_2 is on the order of 1 V vs SCE, there will be no driving force advantage, or at best a small one, for E2 over ET with such reactants.

Reductive elimination of *vic*-dibromoalkanes at a mercury electrode also proceeds in an inner-sphere manner as shown by the fact that the reduction potentials are quite significantly positive to those observed at a carbon electrode (by 190 to 540 mV). The reaction mechanism most probably involves again a bromine or bromonium abstraction occurring at the mercury surface. The stereospecificity experiments seem to fall in line with an E2 mechanism since total selectivity is obtained (Table IV and ref 11b,g). However, a distinction between ET and HA on one hand and E2 on the other as clear-cut as in the case of homogeneous reagents is difficult to reach since stereospecificity is almost complete even in the case of heterogeneous ET, as shown above with glassy carbon. The same is true for gold and platinum cathodes.^{12c,16}

Conclusion

The main conclusions emerging from the preceding results and discussion are as follows.

As a result from the analysis of the kinetic data, outer-sphere reagents such as carbon electrodes and aromatic anion radicals react with vicinal dibromoalkanes according to an "ET" mechanism in which the rate-determining step is a concerted electron-transfer bond-breaking reaction leading to the β -bromoalkyl radical. The latter is then reduced very rapidly, in a second step, most probably along another concerted electron-transfer bond-breaking reaction leading directly to the olefin which offers both a very positive standard potential (on the order of 1 V vs SCE) and a small intrinsic barrier in the heterogeneous case and through halogen-atom expulsion in the homogeneous case. In the absence of steric constraints the reduction goes entirely through the antiperiplanar conformer because the resulting β -bromoalkyl radicals is then stabilized by delocalization of the unpaired electron over the C-C-X framework due to a favorable interaction between the p_z orbital of the radical carbon and the σ^* orbital of the C-Br bond. This interaction is enhanced by alkyl substitution at the reacting carbons, resulting in an approximately linear correlation between the reduction potential and the C-X bond energy of OIX₂ on one hand and the vertical ionization potential of the olefin on

the other. The stabilization energy is on the order of 0.2–0.3 eV for the anti conformers. It can also be taken as a measure of the rotation barrier around the C-C bond responsible for the loss of stereospecificity in the reduction. This competes with the reduction of the two stable conformers of the OIX^{*} radicals. There is a remarkably good agreement between the ensuing prediction of the *E:Z* olefin ratio that should be found upon reduction of *meso*- and *dl*-OIX₂ isomers by outer-sphere reagents such as aromatic anion radicals and the experimental data.

On the other hand although, members of perfectly reversible redox couples, iron(I), iron("0"), and cobalt(I) porphyrins, offer typical examples of inner-sphere reagents in their reaction with vicinal dibromoalkanes. They indeed react much more rapidly than outer-sphere electron donors (aromatic anion radicals) of the same standard potential. On the basis of steric hindrance experiments, it was shown that they do not react according to an S_N2 rate-determining step involving the transient formation of an organometallic species. Total stereospecificity is obtained, showing that they react along a halonium transfer E2 elimination mechanism rather than by an E1 elimination or a halogen-atom transfer mechanism. As shown on a quantitative basis this is related to the large driving force offered to halonium abstraction by the strong affinity of the iron(III) and cobalt(III) complexes toward halide ions.

In regards to catalysis, the investigated systems provide typical examples showing the superiority of inner-sphere (chemical) catalysis over outer-sphere (redox) catalysis of electrochemical reactions. Not only the catalytic efficiency is much better since the rate constants of the key steps are larger, given the standard potential of the catalyst, but also selectivity is dramatically improved.

Experimental Section

Chemicals. The DMF was of commercial origin (Fluka) and was vacuum distilled before use. The supporting electrolytes were purchased (Fluka). Bu₄NPF₆ and Bu₄NClO₄ were twice recrystallized in a mixture of ethanol and ethyl acetate (2/1). The Bu₄NBF₄ was prepared by mixing equimolar aqueous saturated solutions of NaBF₄ and *n*-Bu₄H₂SO₄. The white solid was washed with water and recrystallized two times from water. It was dried at 60 °C over P₄O₁₀. *n*-Decane was gold label quality from Janssen. All olefins with the exception of (*Z*)-4-octene and 3-ethyl-3-hexene were from commercial origin (Fluka, Aldrich, and Janssen) and were used as received. All the mediators, aromatic hydrocarbons, and cobalt and iron porphyrins were from commercial origin with the exception of a-(Cl₂)₂-AC-TPPFe and e-(diC₄Ph)₂-CT-TPPFe which were synthesized according to described procedures.⁴⁵

(*Z*)-4-Octene. (*Z*)-4-Octene was synthesized from 4-octyne by catalytic hydrogenation at normal pressure with a P-2Ni catalyst, ethanol as solvent, and ethylene diamine as a moderator.⁴⁶ *n*-Pentane instead of ether was used for extraction. The yield of (*Z*)-4-octene after fractional distillation (bp 59 °C/100 mm) was 83%. No (*E*)-4-octene could be detected by GC analysis of the product: IR (film) 3020 (s, =C-H), 2950 and 2870 (s, C-H), 1650 (w, C=C), 1455 and 1375 (m, C-H, def), 690 (m, *cis*-HC=CH-, def) cm⁻¹; MS (GC/MS, 70 eV) *m/z* (relative intensity) 112 (24, M⁺), 84 (7), 83 (16), 70 (43), 69 (29), 56 (47), 55 (100); ¹H NMR (CDCl₃, 300 MHz) δ 0.90 (t, 6 H, *J* = 7.3 Hz, 1-H₃ and 8-H₃), 1.37 (sextet, 4 H, *J* = 7.3 Hz, 2-H₂ and 7-H₂), 2.01 (dt, incompletely resolved, 4 H, 3-H₂ and 6-H₂), 5.32–5.42 (m, 2 H, -HC=CH-).

Synthesis of 3-Ethyl-3-hexene. 3-Ethyl-3-hexene was prepared by a Wittig reaction⁴⁷ from 3-pentanone and *n*-propyltriphenylphosphonium bromide. To a stirred suspension of potassium *tert*-butoxide (20.4 mmol) in 95 mL of absolute ether, kept under nitrogen, was added *n*-propyltriphenylphosphonium bromide (20 mmol). The ylid mixture was stirred under reflux for 20 min. After removal of most of the solvent under nitrogen a solution of 19.8 mmol of 3-pentanone in 10 mL of absolute ether was added. The mixture was heated to 40 °C for 4 h and stirred at room temperature overnight. Then the suspension was diluted with 30 mL of *n*-pentane and hydrolyzed by adding 10 mL of water. The organic layer was separated, and the aqueous suspension was extracted three times with 50 mL of *n*-pentane. The combined organic layers were

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washed with water and dried over magnesium sulfate. A fractional distillation under reduced pressure yielded 48% of the desired product with a bp of 60 °C (100 mm) and n_D^{20} of 1.4199 (lit.⁴⁸ bp 116 °C (760 mm), n_D^{20} 1.418); IR (film) 3010 (w, =C-H), 2.70, 2940 and 2870 (s, C-H), 1460 and 1375 (m, C-H, def), 850 (m, R₂C=CRH, def); MS (GC/MS, 70 eV) m/z (relative intensity) 112 (26, M⁺), 97 (3), 83 (82), 69 (15), 55 (100), 41 (66); ¹H NMR (CDCl₃, 300 MHz) δ 0.96/0.97/0.98 (3t, 9 H, $J = 7.6/7.5/7.5$ Hz, 3 CH₃), 1.90–2.10 (m, 6 H, 3 CH₂), 5.06 (t, 1 H, $J = 6.8$ Hz, >C=CH-).

Synthesis of the Dibromoalkanes 1–9, 11, and 12: General Procedure. To a solution of 10 mmol of the corresponding olefin in 30 mL of dichloromethane was added a slight excess of pyridinium hydrobromide-perbromide, prepared according to the method of Fieser and Fieser.⁴⁹ The mixture was stirred for 2 h at 0 °C and for 1 h at room temperature. After addition of aqueous sodium hydrogen sulfite for destruction of the excess reagent, the organic layer was washed four times with 15 mL of water. It was dried over anhydrous sodium sulfate, and the solvent was evaporated at room temperature. The crude product was further purified by filtration over a short silica gel column (diameter 2 cm, length 5 cm) with petroleum ether as eluent. Subsequent distillation under reduced pressure (except for 1, which was recrystallized from ethanol) yielded 51–88% of the corresponding dibromoalkane.

2,3-Dibromo-2,3-dimethylbutane (1): 77%, mp 165 °C (sublimation) (lit.⁵⁰ mp 165–175 °C); ¹H NMR (CDCl₃, 300 MHz) δ 2.02 (s, 12 H, 4 CH₃); MS (GC/MS, 70 eV) m/z (relative intensity) 163/165 (32/31, M⁺ - Br), 121/123 (8/7), 84 (13), 83 (28), 69 (27), 55 (36), 43 (30), 41 (100).

3,4-Dibromo-3-ethylhexane (2): 51%, bp 100 °C (12 mm), n_D^{20} 1.5095; ¹H NMR (CDCl₃, 300 MHz) δ 1.07/1.08/1.25 (3t, 9 H, $J = 7.3/7.3/7.3$ Hz, 3 CH₂), 1.82 (ddd, 1 H, $J = 14.5, 10.9, 7.3$ Hz, 5-H), 2.00 (2dq, 4 H, $J = 22.3, 7.3$ Hz, 2-H₂ and 7-H₂), 2.38 (ddq, 1 H, $J = 14.5, 1.5, 7.3$ Hz, 5-H), 4.14 (dd, 1 H, $J = 10.9, 1.5$ Hz, CHBr); MS (GC/MS, 70 eV) m/z (relative intensity) 191/193 (15/15, M⁺ - Br), 163/165 (1/1), 149/151 (2/2), 135/137 (2/2), 121/123 (2/2), 111 (47), 83 (6), 69 (100), 55 (52), 43 (24), 41 (54). Anal. Calcd for C₈H₁₆Br₂: C, 35.32; H, 5.93; Br, 58.75. Found: C, 35.45; H, 5.94; Br, 58.82.

2,3-Dibromo-2-methylpentane (3): 72%, bp 65–66 °C (15 mm), n_D^{20} 1.5059 (lit.⁵² bp 71–72 °C (18 mm), n_D^{20} 1.5063); ¹H NMR (CDCl₃, 300 MHz) δ 1.14 (t, 3 H, $J = 7.3$ Hz, 5-H₃), 1.80 (ddq, 1 H, $J = 14.5, 11.0, 7.3$ Hz, 4-H), 1.81 (s, 3 H, 1-H₃ or 6-H₃), 1.99 (s, 3 H, 6-H₃ or 1-H₃), 2.48 (ddq, 1 H, $J = 14.5, 1.7, 7.3$ Hz, 4-H), 4.13 (dd, 1 H, $J = 11.0, 1.7$ Hz, CHBr); MS (GC/MS, 70 eV) m/z (relative intensity) 163/165 (37/35, M⁺ - Br), 121/123 (10/10), 107/109 (3/3), 83 (100), 69 (12), 55 (74), 43 (61), 41 (83).

1,2-Dibromo-2-ethylbutane (4): 75%, bp 68.5 °C (16 mm), n_D^{20} 1.5112 (lit.⁵² bp 87 °C (21 mm), n_D^{20} 1.5112); ¹H NMR (CDCl₃, 300 MHz) δ 1.07 (t, 6 H, $J = 7.4$ Hz, 2 CH₃), 1.90/2.00 (2dq, 4 H, $J = 14.8, 7.4$ Hz, 3-H₂ and 5-H₂), 3.38 (s, 2 H, CH₂Br); MS (GC/MS, 70 eV) m/z (relative intensity) 163/165 (13/13, M⁺ - Br), 133/135 (1/1), 121/123 (3/3), 107/109 (2/2), 93/95 (1/1), 83 (84), 69 (12), 55 (100), 43 (46), 41 (82).

1,2-Dibromo-2-methylpentane (5): 60%, bp 69 °C (14 mm), n_D^{20} 1.5020 (lit.⁵² bp 87–88 °C (20 mm), n_D^{20} 1.5015); ¹H NMR (CDCl₃, 300 MHz) δ 0.98 (t, 3 H, $J = 7.3$ Hz, 5-H₃), 1.46–1.60 (m, 2 H, 4-H₂), 1.85 (s, 3 H, 6-H₃), 1.81–1.90 (m, 2 H, 3-H₂), 3.80–3.90 (AB system, $\delta_A = 3.82, \delta_B = 3.88, 2 H, J_{AB} = 10.1$ Hz, CH₂Br); MS (GC/MS, 70 eV) m/z (relative intensity) 163/165 (35/32, M⁺ - Br), 121/123 (7/6), 107/109 (2/2), 93/95 (1/1), 83 (100), 69 (8), 55 (85), 43 (37), 41 (84).

meso-4,5-Dibromooctane (6): 88%, bp 118–119 °C (15 mm), n_D^{20} 1.4990 (lit.⁵³ bp 79–80 °C (4.3 mm), n_D^{20} 1.4967); ¹H NMR (CDCl₃, 300 MHz) δ 0.96 (t, 6 H, $J = 7.4$ Hz, 1-H₃ and 8-H₃), 1.37–1.44 (m, 2 H, 2-H and 7-H), 1.57–1.76 (m, 2 H, 2-H and 7-H), 1.86–2.00 (m, 2 H, 3-H and 6-H), 2.00–2.13 (m, 2 H, 3-H and 6-H), 4.17 (m, 2 H, 4-H and 5-H); GC (GC/MS, 70 eV) m/z (relative intensity) 191/193 (9/9, M⁺ - Br), 149/151 (1/1), 135/137 (2/2), 111 (40), 69 (100), 55 (59), 43 (20), 41 (56).

dl-4,5-Dibromooctane (7): 80%, bp 124 °C (15 mm), n_D^{20} 1.4969 (lit.⁵³ bp 84.0–84.5 °C (4.3 mm), n_D^{20} 1.4981); ¹H NMR (CDCl₃, 300 MHz) δ 0.96 (t, 6 H, $J = 7.3$ Hz, 1-H₃ and 8-H₃), 1.32–1.50 (m, 2 H, 2-H and 7-H), 1.57–1.73 (m, 2 H, 2-H and 7-H), 1.77–1.92 (m, 2 H,

3-H and 6-H), 1.97–2.08 (m, 2 H, 3-H and 6-H), 4.25 (m, 2 H, 4-H and 5-H); GC (GC/MS, 70 eV) m/z (relative intensity) 270/272/274 (0.2/0.4/0.2, M⁺), 191/193 (5/5, M⁺ - Br), 149/151 (1/1), 135/137 (1/1), 111 (52), 69 (100), 55 (55), 43 (11), 41 (36), 39 (10).

erythro-2,3-Dibromohexane (8): 85%, bp 88 °C (15 mm), n_D^{20} 1.5025 (lit.⁵¹ bp 90 °C (16 mm), n_D^{20} 1.5025); ¹H NMR (CDCl₃, 300 MHz) δ 0.96 (t, 3 H, $J = 7.3$ Hz, 6-H₃), 1.37–1.54 (m, 1 H, 5-H), 1.57–1.76 (m, 1 H, 5-H), 1.80–1.96 (m, 1 H, 4-H), 1.87 (d, 3 H, $J = 6.6$ Hz, 1-H₃), 0.27 (dddd, 1 H, $J = 14.6, 10.0, 6.2, 3.1$ Hz, 4-H), 4.13 (ddd, 1 H, $J = 9.1, 7.6, 3.0$ Hz, 3-H), 4.24 (dq, 1 H, $J = 7.6, 6.6$ Hz, 2-H); MS (GC/MS, 70 eV) m/z (relative intensity) 163/165 (25/248 M⁺ - Br), 121/123 (3/2), 107/109 (3/3), 83 (93), 55 (100), 43 (22), 41 (57).

threo-2,3-Dibromohexane (9): 56%, bp 87 °C (15 mm), n_D^{20} 1.5025 (lit.⁵² bp 90 °C (16 mm), n_D^{20} 1.5025); ¹H NMR (CDCl₃, 300 MHz) δ 0.97 (t, 3 H, $J = 7.4$ Hz, 6-H₃), 1.32–1.51 (m, 1 H, 5-H), 1.56–1.74 (m, 1 H, 5-H), 1.74–1.88 (m, 1 H, 4-H), 1.77 (d, 3 H, $J = 6.7$ Hz, 1-H), 2.03 (dddd, 1 H, $J = 14.5, 9.6, 6.5, 3.0$ Hz, 4-H), 4.22 (ddd, 1 H, $J = 10.3, 3.0, 3.0$ Hz, 3-H), 4.45 (dq, 1 H, $J = 3.0, 6.7$ Hz, 2-H); MS (GC/MS, 70 eV) m/z (relative intensity) 242/244/246 (0.5/1.0/0.4, M⁺), 163/165 (24/23, M⁺ - Br), 121/123 (3/3), 107/109 (3/3), 83 (91), 55 (100), 43 (26), 41 (60).

1,2-Dibromooctane (11): 60%, bp 112 °C (12 mm), n_D^{20} 1.4969 (lit.⁵⁵ bp 118.5 °C (15 mm), n_D^{20} 1.4970); ¹H NMR (CDCl₃, 300 MHz) δ 0.90 (t, 3 H, $J = 6.7$ Hz, 8-H₃), 1.20–1.64 (m, 8 H, 4-H₂ to 7-H₂), 1.79 (dddd, 1 H, $J = 14.4, 14.4, 9.8, 4.8$ Hz, 3-H), 2.14 (dddd, 1 H, $J = 14.4, 10.1, 5.6, 3.2$ Hz, 3-H), 3.63 (dd, 1 H, $J = 10.1, 10.1$ Hz, 1-H), 3.85 (dd, 1 H, $J = 10.1, 4.4$ Hz, 1-H), 4.17 (m, 1 H, 2-H); MS (GC/MS, 70 eV) m/z (relative intensity) 227/229/231 (0.1/0.2/0.1, M⁺ - C₃H₇), 191/193 (7/7, M⁺ - Br), 149/151 (7/6), 135/137 (6/6), 121/123 (3/2), 111 (50), 69 (100), 55 (57), 43 (68), 41 (76).

1,2-Dibromopentane (12): 80%, bp 69 °C (14 mm), n_D^{20} 1.5060 (lit.⁵⁶ bp 72–74 °C (15 mm), n_D^{20} 1.5063); ¹H NMR (CDCl₃, 300 MHz) δ 0.96 (t, 3 H, $J = 7.3$ Hz, 5-H₃), 1.36–1.70 (m, 2 H, 4-H₂), 1.70–1.86 (m, 1 H, 3-H), 2.11 (dddd, 1 H, $J = 14.6, 9.7, 6.2, 3.9$ Hz, 3-H), 3.63 (dd, 1 H, $J = 10.1, 10.1$ Hz, 1-H), 3.85 (dd, 1 H, $J = 10.1, 4.4$ Hz, 1-H), 4.81 (dddd, 1 H, $J = 10.1, 9.5, 4.4, 3.3$ Hz, 2-H); MS (GC/MS, 70 eV) m/z (relative intensity) 228/230/232 (0.1/0.2/0.1, M⁺), 149/151 (24/23, M⁺ - Br), 107/109 (4/4), 69 (100), 43 (15), 41 (80).

Synthesis and Separation of the Dibromoalkanes 14 and 15. 3(a),4-(a)-Dibromo-1(e)-methylcyclohexane (14) and 3(e),4(e)-dibromo-1(e)-methylcyclohexane (15) were obtained as a mixture of isomers (90% 14 and 10% 15) from the bromination of 4-methylcyclohexene with bromine in CHCl₃ at 0 °C⁵⁷ (total yield 89%). The separation of 14 and 15 by flash column chromatography with petroleum ether as eluent⁵⁸ yielded 82% of 14 and 5% of 15. Purity was checked by NMR.

3(a),4(a)-Dibromo-1(e)-methylcyclohexane (14): ¹H NMR (CDCl₃, 300 MHz) δ 0.96 (d, 3 H, $J = 6.3$ Hz, CH₃), 1.45–1.63 (m, 2 H), 1.85–2.18 (m, 4 H), 2.40–2.54 (m, 1 H), 4.62–4.72 (m, 2 H, -HBrC-CBrH-, equatorial H); MS (GC/MS, 70 eV) m/z (relative intensity) 254/256/258 (0.3/0.6/0.3, M⁺), 175/177 (4/4, M⁺ - Br), 133/135 (1/1), 119/121 (2/2), 96 (10), 95 (100), 67 (16), 55 (12), 41 (10), 39 (11).

3(e),4(e)-Dibromo-1(e)-methylcyclohexane (15): ¹H NMR (CDCl₃, 300 MHz) δ 0.93 (d, 3 H, $J = 6.1$ Hz, CH₃), 1.00–1.20 (m, 1 H), 1.50–1.79 (m, 3 H), 1.83–2.00 (m, 1 H), 2.38–2.52 (m, 2 H), 3.94–4.12 (m, 2 H, -HBrC-CBrH-, axial H); MS (GC/MS, 70 eV) m/z (relative intensity) 254/256/258 (0.5/1.0/0.5, M⁺), 175/177 (4/4, M⁺ - Br), 133/135 (1/1), 119/121 (2/2), 96 (8), 95 (100), 67 (14), 55 (11), 53 (7), 41 (8), 39 (9).

Instrumentation. GC analysis was performed on a Shimadzu GC-14A chromatograph combined with a Shimadzu C-R6A integrator and plotter. IR spectra were taken on a Shimadzu IR-408 spectrometer. ¹H NMR spectroscopy was done on a Bruker WM 300 instrument, and GC/MS analysis was performed on a Varian-MAT 111 (70 eV) with a capillary GC/MS CH7A combined with a data system SS 200 from Finnigan-MAT.

Preparative Scale Electrolyses. Instrumentation. For preparative scale electrolyses a small, gas-tight cell with two 10-mL compartments divided by a G3 sintered glass frit was used. The anode compartment was equipped with a magnesium ribbon counter electrode. The cathode compartment contained a magnetic stirring bar, a Marple⁵⁹ reference

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electrode with Luggin capillary, and an argon in- and outlet port, consisting of a septum with two syringe needles. The working electrode was either a glassy carbon disk of 6-mm diameter, carefully polished before use, or a carbon rod of 7-mm height and 8-mm diameter, employed in the mediated electrolyses. A disk of 6-mm diameter of amalgamated gold was used as a mercury working electrode. It was prepared by galvanostatic electrolysis of an aqueous solution of 0.1 M $\text{Hg}(\text{NO}_3)_2$ with the gold electrode as cathode and a platinum anode. A current of 10 mA was applied to the cell for 2 min, and the electrode was subsequently washed with dry DMF before use. The cell was immersed in a water bath to keep it at 20 °C.

The electrolyses were carried out with a Wenking potentiostat 68 FR 0.5 from Bank Elektronik. The charge was counted by a calibrated direct current integrator. The working potential was controlled with a Fluke digital multimeter.

Procedures of Electrolyses. All operations were carried out after removal of dioxygen by argon or nitrogen bubbling.

1. Direct electrolyses at glassy carbon or amalgamated gold: the empty cell was heated and degassed with argon for 15 min. Each of the cell compartments was then filled with 7 mL of the degassed 0.1 M solution of Bu_4NBF_4 in DMF, and the background current was determined. After addition of 0.4 mmol of the substrate and 44.6 mg of *n*-decane, used as internal standard, the catholyte was vigorously stirred for 15 min. Before starting the electrolysis a 0.1-mL probe of the catholyte was taken to determine the concentration of the starting compound at the beginning. The electrolyses were stopped when no starting material could be detected by GC analysis.

2. Indirect electrolyses with 1,4-diacetylbenzene as mediator: the procedure was the same as for the direct electrolyses with one exception—before addition of the dibromoalkane and the internal standard 0.4 mmol of the mediator was dissolved in the DMF solution, and the background current of the catalyst was determined.

3. Indirect electrolyses with metalloporphyrin mediators: 0.01 mmol of the mediator was dissolved in 5 mL of the degassed 0.1 M Bu_4NBF_4 /DMF solution under argon with vigorous stirring. This solu-

tion was transferred into the cathode compartment of the degassed cell. The emptied flask was rinsed two times with 1 mL of the solvent, which were also transferred into the cathode compartment. The anode compartment was filled with 8 mL of the electrolyte solution and a cyclic voltammogram was taken to control the absence of oxygen. Then 0.4 mmol of the substrate and 44.6 mg of *n*-decane were added and after taking the first sample the electrolysis was started. It was stopped when the current had decreased to 1–3%.

Analysis. To remove DMF and the supporting electrolyte the electrolysis probes were filtered through a Pasteur pipette half-filled with flash silica gel (Merck). Five milliliters of *n*-pentane were taken as eluent. The resulting solutions were analyzed by GC by using a quartz capillary column (FS-SE54-CB 0.25 μ , 50-m length). *n*-Decane was employed as internal standard to determine the yield of the olefins and the dibromoalkanes. The different compounds were identified by comparison of their retention times and their MS spectra with those of authentic samples.

Differential Pulse Polarography. Instrumentation. Differential pulse polarography was performed with the Bruker Polarograph E310 in combination with the Metrohm polarographic equipment E354. The recording of the polarograms was done on a Hewlett-Packard XY-writer 7044A in a Metrohm cell (EA876). It was equipped with a platinum foil counter electrode of 1 cm², a saturated calomel reference electrode with Luggin capillary, and a nitrogen in- and outlet.

Procedures. Twenty milliliters of a degassed 4×10^{-4} M solution of the dibromoalkane in 0.1 M Bu_4NBF_4 /DMF were examined under the following conditions: drop time, 1 s; sweep rate, 5 mV/s; differential pulse amplitude, 50 mV; room temperature.

Cyclic Voltammetry. The instrumentation, cell, electrodes, and procedures were the same as previously described.^{12a}

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Surface Raman Scattering of Methanol, 1-Propanol, 1-Pentanol, and 1-Butanethiol on in Situ and Emerged Silver Electrodes

Raymond L. Sobocinski, Mark A. Bryant, and Jeanne E. Pemberton*

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721. Received January 18, 1990

Abstract: Surface Raman scattering is used to study the adsorption of several straight-chain alcohols (methanol, 1-propanol, 1-pentanol) and a straight-chain alkanethiol (1-butanethiol) at Ag electrodes. Surface-enhanced Raman scattering (SERS) studies are carried out on both in situ and emerged roughened electrodes. Normal surface Raman scattering is performed on mechanically polished, mirrored polycrystalline electrodes that have been emerged from solution. It is generally observed that the Raman scattering results, in terms of the orientation and bonding for the alcohols and the thiol, are similar on rough and mirrored electrodes. This observation suggests that SERS probes the average surface molecules in these cases and not only those existing at chemically distinct surface sites. The utility of emerged electrode approaches for molecular characterization of the electrochemical interface is demonstrated for these systems. The interfacial molecular structure for these in situ organic species appears to be maintained upon emersion.

Introduction

Considerable recent effort has been focused on elucidating the factors that impact the efficiency of electron transfer between a metal electrode and a solution-confined redox species. Toward this end, a detailed description of the molecular characteristics of the interface that develops upon immersion of a metal electrode

into an electrolyte solution has been sought. A variety of spectroscopic methods have been applied to the investigation of this problem. Of these, Raman scattering has been demonstrated to be a particularly attractive probe of these systems due to the sensitivity of molecular vibrations to chemical environment.

One Raman spectroscopic approach for the investigation of these interfaces that has received intensive study is surface-enhanced Raman scattering (SERS). As a result of the ca. 10^4 to

* Author to whom correspondence should be addressed.