

Electroreduction of Dialkyl Peroxides. Activation–Driving Force Relationships and Bond Dissociation Free Energies^{1a}

Sabrina Antonello,^{1b} Martin Musumeci,^{1b,c} Danial D. M. Wayner,^{1d} and Flavio Maran^{*,1b}

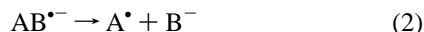
Contribution from the Dipartimento di Chimica Fisica, Università di Padova, via Loredan 2, 35131 Padova, Italy, and the Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6

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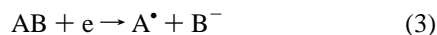
Abstract: The electrochemical reduction of five dialkyl peroxides in DMF was studied by cyclic voltammetry. The electron transfer (ET) to the selected compounds is concerted with the oxygen–oxygen bond cleavage (dissociative ET) and is independent of the electrode material. Such an electrochemical behavior provided the opportunity to study dissociative ETs by using the mercury electrode and therefore to test the dissociative ET theory by using heterogeneous activation–driving force relationships. The convolution voltammetry analysis coupled to the double-layer correction led to reasonable estimates of the standard potential (E°) for the dissociative ET to dialkyl peroxides, as supported, whenever possible, by independent estimates. A thermochemical cycle based on the dissociative ET concept was employed to calculate the bond dissociation free energies (BDFEs) of the five peroxides, using the above E° s together with electrochemical or thermochemical data pertaining to the redox properties of the leaving alkoxide ion. The BDFEs were found to be in the 25–32 kcal/mol range, suggesting a small substituent effect. The dissociative ET E° s were also used together with the experimental quadratic free energy relationships to estimate the heterogeneous reorganization energies.

Introduction

Radical anion formation by electron transfer (ET) to an organic molecule AB (eq 1) can be followed by an irreversible bond-breaking reaction (eq 2) leading to a radical, A^\bullet , and an anion, B^- ,² where the intermediate species $AB^{\bullet-}$ may fragment



with rates which can vary over a wide range. However, when the lifetime of the radical anion is so short to be of the same order of magnitude as that of the vibration of the bond which is going to be broken, there is no bound state for $AB^{\bullet-}$. The ET can no longer be considered as an outer sphere process³ and is now best described as taking place in the single step (eq 3) and referred to as dissociative ET. The theory for such a



concerted mechanism has been described by Savéant, who considered the adiabatic aspects of this reaction.⁴ More recently a corresponding nonadiabatic treatment has been proposed.⁵ In

the classical limit, where Morse-like potential energy curves are adopted to describe reagents and products of the ET and the harmonic approximation is used to describe activation by the solvent, the development of the model leads to the formulation of a simple Marcus-like activation–driving force relationship in which the activation free energy ΔG^\ddagger depends quadratically on the free energy ΔG° of the reaction, according to eq 4:⁴

$$\Delta G^\ddagger = \Delta G_0^\ddagger \left(1 + \frac{\Delta G^\circ}{4\Delta G_0^\ddagger} \right)^2 \quad (4)$$

The intrinsic barrier ΔG_0^\ddagger , i.e. the activation free energy at zero driving force, is given by three contributions: two of them are the outer or solvent reorganization λ_o and the inner reorganization λ_i , where the latter term does not include the contribution of the mode corresponding to the breaking A–B bond; the third, very important term is the bond dissociation energy, BDE. Accordingly,

$$\Delta G_0^\ddagger = \frac{\lambda_o + \lambda_i + \text{BDE}}{4} \quad (5)$$

Whereas there is a wide literature concerning stepwise reductive cleavages, either thermally induced or photoinitiated,² the number of investigations on dissociative ETs is still limited. The dissociative ET mechanism has been studied in dipolar aprotic solvents by using either inert electrodes or aromatic radical anions as electron donors. Specific, relevant examples concern the dissociative reduction of alkyl^{6,7} or benzyl halides,^{8,9}

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(1) (a) Issued as NRCC publication No. 40836. (b) Università di Padova. (c) Permanent address: Chemistry Department, Junior College, University of Malta, Msida, Malta. (d) National Research Council of Canada.

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and therefore the cleavage of C–halogen bonds, the cleavage of the C–S bond in sulfur compounds,^{10,11} and the cleavage of O–O bonds in peroxides.¹² From a quantitative point of view, the dissociative ET theory has been tested rather satisfactorily^{4b,13,14} through comparison of experimental data pertaining to the reduction of methyl, butyl, and benzyl halides, with theoretical predictions.

One of the most relevant problems is the difficulty of estimating the standard potential for the dissociative process 3; since the direct determination of this potential is unfeasible, thermochemical data, such as the bond dissociation energy of the A–B bond, are required. Such data may not be easily available and are often approximate, for example, due to the use of bond dissociation enthalpies instead of free energies. Furthermore, the evidence for a quadratic activation–driving force relationship, which is quite important in the analysis of a dissociative ET process, is not clear-cut in some cases, such as in, for example, the homogeneous reduction of *tert*-butyl bromide, for which data are available for an overall variation of the rate constant by 13 orders of magnitude.¹⁵ In other reactions, the experimental data fit equally well to a parabola or to a straight line, a matter that leads to discussion.^{13,15} From a practical point of view, this is not a trivial aspect; for example, it is impossible to use the rate data to trace back the unknown standard potential of the acceptor AB molecule from a linear activation–driving force relationship. On the contrary, this target is reachable if a quadratic activation–driving force relationship is beyond experimental error. As a matter of fact, it should be noticed that the curvature of the parabola described by eq 4, given by

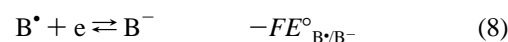
$$\frac{\partial^2 \Delta G^\ddagger}{\partial \Delta G^\circ{}^2} = \frac{1}{8\Delta G_0^\ddagger} \quad (6)$$

is smaller the larger ΔG_0^\ddagger is, which is a very common situation in dissociative ETs owing to the weight of the BDE term in eq 5.

The calculation of bond energies in solution is particularly important.¹⁶ In principle, when the dissociative nature of the ET is assessed, this could be done by using experimental rate data and comparing them with theoretical rate constants. This requires that a value for the pre-exponential factor describing the rate constant itself has to be assumed followed by the use of eq 4 to obtain the BDE. What is needed is the reorganization energy, with the problems associated with the calculation of the λ_o and λ_i terms, and the free energy of the reaction. This possible application of the dissociative ET theory has been stressed.^{2d} To calculate the BDE in this way, however, the degree of adiabaticity of the ET step must be known. Very recently, using data on the reduction of di-*tert*-butyl peroxide and dicumyl peroxide in DMF and MeCN, we found that serious

errors can arise if the ET rate results are used to obtain bond energies in solution.¹² The ET to the above peroxides was studied by using a family of aromatic electron donors, and the experimental rates were found to be significantly smaller than predicted by the theory of adiabatic dissociative ET.^{4b} The reasons for such a discrepancy were explained partly through the presence of steric hindrance caused by the *tert*-butyl and cumyl groups and partly due to an intrinsic nonadiabaticity of the ET.

In this paper we examine the possibility of using ET rate data to obtain the bond dissociation free energies (BDFEs) for dissociative ETs using a different approach to avoid the above difficulties. As mentioned above, due to the reaction being completely irreversible, the standard potential for a dissociative ET cannot be calculated directly, say, by cyclic voltammetry; however, it can be conveniently calculated by using the following thermodynamical cycle¹⁷



and therefore through the equation:

$$E_{AB/A^\bullet, B^-}^\circ = E_{B^\bullet/B^-}^\circ - \text{BDFE}/F \quad (10)$$

If the aim is to estimate $E_{AB/A^\bullet, B^-}^\circ$, the problem is to have good experimental data or estimates for the two terms on the right-hand side of eq 10.^{12a} Conversely, if one can obtain $E_{AB/A^\bullet, B^-}^\circ$ through the activation–driving force relationship for the investigated process, a powerful tool is provided to calculate BDFEs once E_{B^\bullet/B^-}° can be estimated or experimentally determined. It is worth noting that in this approach neither the internal and solvent reorganization energies nor the knowledge of the degree of adiabaticity of the ET reaction are required.

In principle, activation–driving force relationships can be obtained by using either direct electrochemical reduction or homogeneous reduction carried out by soluble one-electron donors. There are however two reasons to prefer an electrode as the electron donor instead of a soluble species. The first reason is that whereas in the heterogeneous case the reorganization energy $\lambda = \lambda_o + \lambda_i$ is dependent only on the acceptor molecule, the homogeneous λ depends also upon the dimension and structure of the one-electron donor; since the curvature of the activation–driving force relationship is given by eq 6, the local curvature is dependent upon the donor. The second reason is that in the heterogeneous approach the free energy of the reaction, i.e. the applied potential, can be varied continuously, and as a result the quantity of data that can be collected is significantly larger.

There is, however, a severe drawback that, until now, precluded the possible use of direct electrochemistry in the determination of BDFEs. In general, when the electron donor is an electrode instead of a soluble species, eq 4 is best written as

$$\Delta G^\ddagger = \Delta G_0^\ddagger \left(1 + F \frac{E - E^\circ - \phi^\ddagger}{4\Delta G_0^\ddagger} \right)^2 \quad (11)$$

where E and E° are the applied and the standard potential, respectively, and ϕ^\ddagger is the difference between the potential at the average distance at which the substrate is located when the

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ET takes place and the potential of the bulk solution. Problems are associated with the knowledge of ϕ^\ddagger and of its derivative $\partial\phi^\ddagger(E)/\partial E$. The fact is that inert electrodes are required to analyze heterogeneous ETs, and this is particularly true when the determination of the kinetics of a dissociative ET is the goal. From a practical point of view the electrode material that minimizes the possible interaction between the electrode and the electroactive dissociative-type substrate or its reduction intermediates is glassy carbon;^{6,8,11,12} unfortunately, the double layer properties of glassy carbon are almost unknown,¹⁸ although some research is being devoted in this direction.¹⁹ On the other hand, the electrode material that has been best characterized from such a point of view is mercury; until now, however, the mercury electrode could never have been used in such studies because it is far from being inert with respect to typical dissociative ET systems, such as the halides.

In this paper the first use of mercury as an inert electrode material in the reduction of dissociative-type substrates is reported. The heterogeneous reduction of a series of dialkyl peroxides has been investigated by cyclic voltammetry in *N,N*-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium perchlorate (TBAP); the selected peroxides were either symmetrical molecules such as di-*tert*-butyl peroxide (DBP), dicumyl peroxide (DCP), and bis(triphenylmethyl) peroxide (DTP) or unsymmetrical ones such as *tert*-butyl triphenylmethyl peroxide (BTP) and cumyl triphenylmethyl peroxide (CTP). It will be shown that the dissociative ET theory works pretty well when the activation-driving force relationship is obtained by using a well-defined experimental procedure and the data are analyzed by the convolution approach coupled to the double layer correction. In this way and through comparison with literature thermochemical data, good estimates of the standard potential and the BDFE can be obtained.

Experimental Section

Chemicals. *N,N*-Dimethylformamide (Janssen, 99%) was treated for some days with anhydrous Na₂CO₃, under stirring, and then distilled at reduced pressure (17 mmHg) under a nitrogen atmosphere. The solvent was collected and stored under an argon atmosphere in dark bottles; it was used only after having checked the absence of electroactive impurities in the available potential window. The supporting electrolyte was tetrabutylammonium perchlorate (99%, Fluka) that was recrystallized from a 2:1 ethanol-water solution and dried at 60 °C under vacuum. Dicumyl peroxide (98%, Aldrich) was recrystallized from ethanol. Di-*tert*-butyl peroxide (98%, Aldrich) was used as purchased. Bis(triphenylmethyl) peroxide was prepared by reaction of triphenylmethyl chloride (Baker) with mercury followed by exposure to air.²⁰

***tert*-Butyl triphenylmethyl peroxide** was prepared as described in the literature,²¹ from triphenylmethanol and *tert*-butyl trimethylsilyl peroxide in an acidic medium. The product had the same melting point as reported,²¹ 69–71 °C, and *R*_f 0.70 (toluene). ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.01 (9H, s, *t*-Bu), 7.25–7.38 (15H, m, 3Ph).

Cumyl triphenylmethyl peroxide was prepared by reacting triphenylmethanol (Aldrich) with cumyl hydroperoxide (80% in cumene, Fluka) in acidic conditions.²² The crude product was dissolved in diethyl ether, treated with sodium hydrogen carbonate and brine, and eventually dried (MgSO₄). The resulting solution was concentrated and the product chromatographed on a silica gel column with toluene and recrystallized from ethanol to give cumyl triphenylmethyl peroxide as colorless crystals having *R*_f 0.87 (toluene-ethyl acetate 10:1) and

mp = 72–74 °C (lit.²² mp 168–169 °C). ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.26 (6H, s, 2Me), 7.1–7.3 (20H, m, 4Ph); ¹³C NMR (400 MHz, CDCl₃, TMS) δ 28.36 (Me), 82.64 (CMe₂), 90.92 (CPh₃), 125.36, 126.57, 127.67, 145.64 (PhCMe₂: C2, C4, C3, C1), 126.97, 127.20, 129.18, 143.25 (Ph₃C: C4, C3, C2, C1).

Electrodes. The working electrode materials were either glassy carbon or mercury. The glassy carbon electrode was built from a 3 mm length by 3 mm diameter glassy carbon rod (Tokai GC-20), sealed in glass tubing. The disk electrode surface was then polished by using silicon carbide papers (500, 1000, 2400, and 4000) and then diamond pastes (Struers: 3, 1, and 0.25 μ m). The electrode was stored in ethanol. Before each measurement, the working electrode was polished with the 0.25 μ m diamond paste and ultrasonically rinsed with ethanol for 5 min. Electrochemical activation was carried out in the background solution by means of several cycles at 0.5 V s⁻¹ between 0 and -2.8 V against the KCl saturated calomel electrode, SCE. In this way the surface was checked to be clean and reproducible. The area was calculated with reference to the diffusion coefficient of anthracene in DMF/0.1 M TBAP, 7.8×10^{-6} cm² s⁻¹.²³ As expected for a microdisk electrode, the area proved to be quite constant, as checked in separate experiments.

The mercury electrode was prepared by controlled electrodeposition of mercury onto a platinum bead substrate. Full details of this procedure are given in the Supporting Information. The particular method employed leads to very stable Hg electrodes which can be used for several years without problems. No effect due to the platinum underneath was ever detected and the heterogeneous ET kinetics of suitable test substrates proved to be those of a bulk mercury electrode. Electrochemical activation was carried out in the background solution by means of several cycles at 0.5 V s⁻¹ between -0.5 and -2.7 V vs SCE.

The reference electrode was a home-made Ag/AgCl.²⁴ Its potential, which is about -0.30 V vs SCE, was always calibrated after each experiment by adding ferrocene as an internal standard; the ferrocene/ferricinium couple is known to be a recommended redox reference system for nonaqueous measurements.²⁵ Our own calibrations (statistics of ca. 50 independent experiments) indicated that the standard potential for ferrocene oxidation in DMF/0.1 M (and 0.2 M) TBAP is 0.464 V vs SCE. In the following, all of the potential values will be reported against SCE. The counter-electrode was a 1 cm² Pt plate, positioned symmetrically under the working electrode.

Electrochemical Apparatus and Procedures. The electrochemical instrumentation employed for cyclic voltammetry was an EG&G-PARC 173/179 potentiostat-digital coulometer, an EG&G-PARC 175 universal programmer, a Nicolet 3091 12-bit resolution digital oscilloscope, and an Amel 863 X/Y pen recorder. The feedback correction was applied to minimize the ohmic drop between the working and reference electrodes. The confidence in the correction was judged by using the same setup, including the working and reference electrode, to check the voltammetric behavior of a redox couple of known heterogeneous kinetics, such as 2-nitro-2-methylpropane; when the IR compensation was properly adjusted, the scan rate dependence of the redox peak was as expected on the basis of our own¹⁹ and literature results.²⁶

Electrochemical measurements were conducted in an all glass cell, thermostated at 25 \pm 0.2 °C. The solution was carefully deoxygenated with Argon (SIAD, 99.9995%), and then a blanket of gas was maintained over the liquid. After deoxygenation, the behavior of the electrode was studied in the background solution, in a selected potential range and for scan rates ranging usually from 0.1 to 100 V s⁻¹. To reduce the electrical noise, the electrochemical measurements were carried out by using a line transformer, doubly shielded coaxial cables for the electrical connections, and, most important, a special copper Faraday cage, designed and optimized to reduce to minimum the high-frequency noise components. The cyclic voltammograms were recorded by the digital oscilloscope and then transferred to a PC. The substrate was

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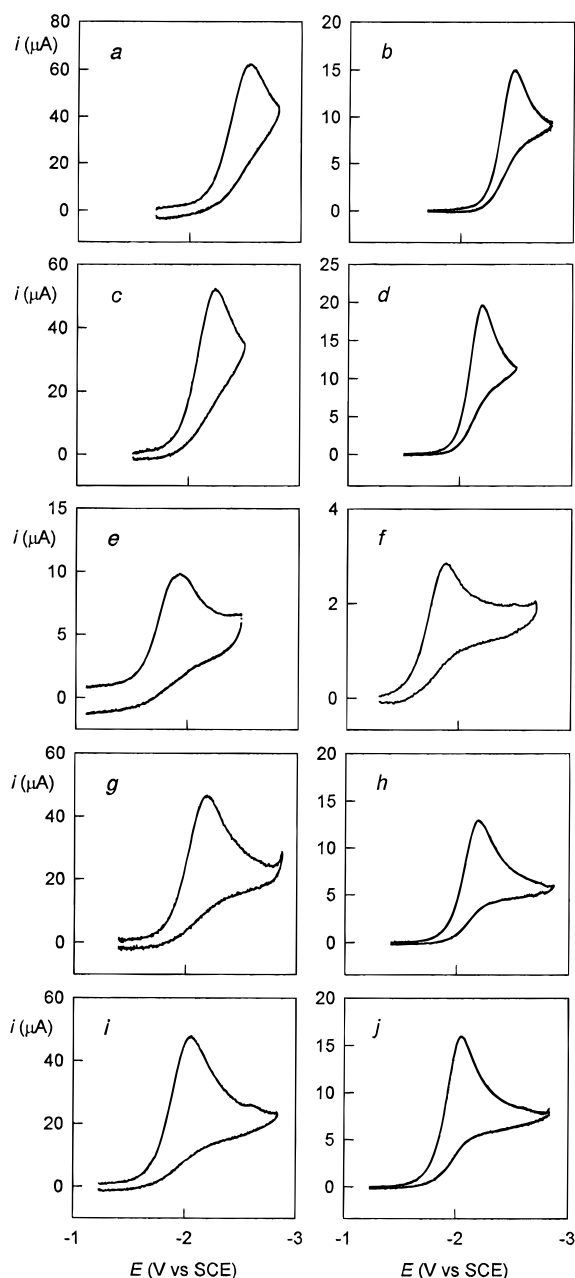


Figure 1. Cyclic voltammetry for the reduction of DBP (a: 2.87 mM, GC; b: 2.18 mM, Hg), DCP (c: 2.10 mM, GC; d: 2.10 mM, Hg), DTP (e: 0.49 mM, GC; f: 0.52 mM, Hg), BTP (g: 2.03 mM, GC; h: 1.89 mM, Hg), and CTP (i: 2.16 mM, GC; j: 2.16 mM, Hg). Whereas curves b–j were obtained in DMF/0.1 M TBAP, curve a was obtained in DMF/0.1 M TEAP. $T = 25\text{ }^{\circ}\text{C}$, $\nu = 0.2\text{ V s}^{-1}$.

then added to the solution and the same procedure repeated. The corresponding background curves were subtracted from the cyclic voltammograms to eliminate the contribution of the capacitive current. The resulting curves were then analyzed by the conventional voltammetric criteria²⁷ and the convolution approach,²⁸ using specially designed laboratory software.

Results and Discussion

The reduction of the selected dialkyl peroxides was studied in DMF/0.1 M TBAP at $25\text{ }^{\circ}\text{C}$ by cyclic voltammetry, using both glassy carbon and mercury as electrode materials. The cyclic voltammograms corresponding to DBP, DCP, DTP, BTP,

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Table 1. Voltammetric Data for the Reduction of Dialkyl Peroxides in DMF/0.1 M TBAP at 0.2 V s^{-1} and $T = 25\text{ }^{\circ}\text{C}$

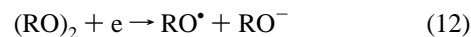
substrate	$E_p(\text{GC})^{a,b}$ (V)	$\Delta E_{p/2}(\text{GC})^{a,c}$ (V)	$E_p(\text{Hg})^b$ (V)	$\Delta E_{p/2}(\text{Hg})^c$ (V)
DBP	-2.50 ^{d,e}	0.188 ^{d,e}	-2.47	0.130
DCP	-2.23	0.158	-2.22	0.128
DTP	-1.91	0.189	-1.89	0.178
BTP	-2.18	0.174	-2.19	0.150
CTP	-2.04	0.185	-2.04	0.147

^a GC = glassy carbon. ^b Potentials are against SCE. ^c $\Delta E_{p/2}$ = peak width. ^d Reference 12a. ^e DMF/0.1 M Et₄NClO₄; see ref 29.

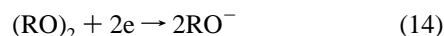
and CTP are shown in Figure 1. As expected for the reduction of dialkyl peroxides in dipolar aprotic solvents,¹² the peaks are located at potentials which are close to or more negative than -2 V . A common feature of the voltammetric pattern is the presence of an irreversible, broad peak. In Table 1 some voltammetric data obtained by averaging the results of different experiments performed at 0.2 V s^{-1} with either electrode are reported. Comparison of the data reveals that no appreciable effects can be ascribed to the electrode material; for a given compound, the peak potentials (E_p) are equal within 10–30 mV and the peak widths, i.e., the differences between the potential measured at half-peak height and E_p ($\Delta E_{p/2}$), are large and usually equal within 10–20%.²⁹ These observations, in particular the position of the peak, are worth noting because the investigated systems appear to provide the first experimental cases in which substrates undergoing a dissociative ET do not interact with mercury.

Since one of the goals of the present work was to calculate the standard potential for the dissociative ET process by accurate analysis of the voltammetric data, the best test to verify the reliability of the adopted approach was to focus initially on dialkyl peroxides for which independent estimates of the standard potential itself were available. Among the investigated substrates, we had previously obtained reasonable estimates of the standard potential of DBP, -1.44 V , and DCP, -1.29 V .¹² Such values were obtained through eq 10 by using thermochemical and electrochemical data and are valid for DMF as the solvent. Preliminary experiments, however, revealed that the voltammetric data pertaining to DBP were not ideal to perform an accurate kinetic analysis because of the proximity of the reduction process to the onset of the solvent/electrolyte breakdown and therefore DCP was chosen as the model compound.

Previous results obtained by using a glassy carbon electrode in DMF/0.1 M Et₄NClO₄^{12b} indicated that the reduction takes place according to the two-step process



and therefore to the overall stoichiometry



where $\text{R} = \text{CMe}_2\text{Ph}$. In the present study, the reduction of DCP was studied at the mercury electrode, using voltammetric scan

(29) The only apparent exception to this trend is provided by the results obtained with DBP because whereas at mercury we obtained a well-behaved pattern, the reduction is more sluggish at the glassy carbon electrode. Apparently, however, this problem is caused by the TBAP electrolyte at such negative potentials because the corresponding curves obtained with the two electrodes in the presence of Et₄NClO₄ are very similar to each other. In fact, the results obtained at the Hg electrode in the presence of either electrolyte are identical.

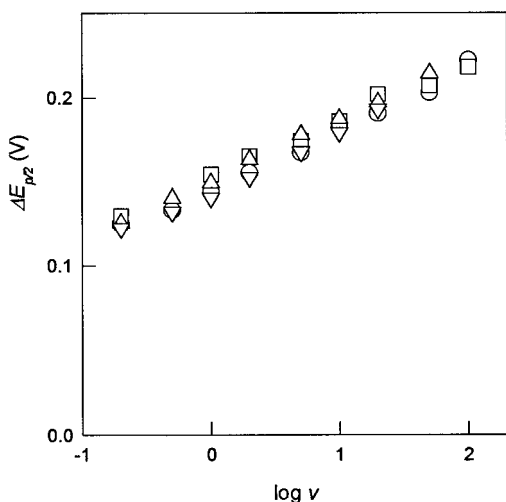


Figure 2. Scan rate dependence of the voltammetric peak width for the reduction of DCP in DMF/0.1 M TBAP at the Hg electrode. Substrate concentration (mM): ○, 2.05; □, 2.09; △, 1.95; ▽, 2.10. $T = 25\text{ }^{\circ}\text{C}$.

rates ranging from 0.2 to 50 V s^{-1} . The process was investigated in DMF/0.1 M TBAP to use available double layer data.³⁰

The reduction peak of DCP is irreversible at all of the scan rates used, and its peak potential shifts toward more negative potentials by increasing the scan rate, ν , the average slope being $166\text{ mV}/\log \nu$. The peak width $\Delta E_{p/2}$ is also scan rate dependent as shown in Figure 2, which derives from separate experiments; for example, whereas the average $\Delta E_{p/2}$ at 0.2 V s^{-1} is 128 mV , it increases to 199 mV when $\nu = 20\text{ V s}^{-1}$. Finally, the ratio between the peak current i_p and $C^*\nu^{1/2}$, where C^* is the bulk concentration, tends to decrease upon increasing ν . The above observations indicate that the heterogeneous ET to DCP cannot be described by a rate law of the Butler–Volmer form,³¹ according to which $\partial E_p/\partial \log \nu$, $\Delta E_{p/2}$, and $i_p/C^*\nu^{1/2}$ should be independent of ν for a completely irreversible electrode process.²⁷

The reasons for such deviations can be ascribed to the non-constancy of the heterogeneous transfer coefficient α with respect to the potential,³² where α is defined as

$$\alpha = \frac{\partial \Delta G^\ddagger}{\partial \Delta G^\circ} \quad (15)$$

Whereas in Butler–Volmer kinetics α is independent of the potential, a decrease of α with a negative increase of the potential would indeed account for the observed behavior. In fact, an irreversible voltammetric peak shifts toward more negative potentials upon increasing the scan rate, and therefore the peak width and current reflect what happens at different potential regions. The peak width is a particularly sensitive detector for a possible potential dependence of α ; in the present case its values, which can be estimated by using the equation $\alpha = 1.857RT/F\Delta E_{p/2}$,²⁷ are e.g. 0.373 at 0.2 V s^{-1} and 0.240 at 20 V s^{-1} . For the sake of argument, if one assumes rather arbitrarily that the potential coordinate for a given α value is

(30) Arévalo, M. C.; Rodríguez, J. L.; Severin, M. G.; Vianello, E. Unpublished results.

(31) Butler, J. A. V. *Trans. Faraday Soc.* **1924**, *19*, 734. Erdey-Gruz, T.; Volmer, M. Z. *Phys. Chem.* **1930**, *150A*, 203.

(32) Although analogous effects might be caused by improper compensation for the ohmic drop, this possibility was ruled out in our experimental conditions thanks to the parallel experiments that we run using redox couples of known heterogeneous kinetics.

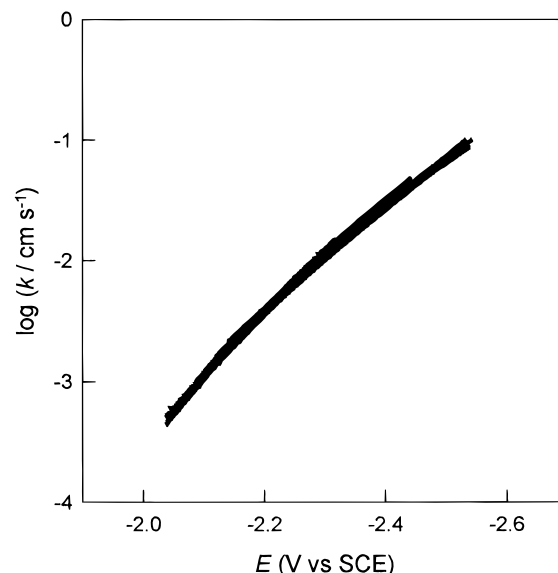


Figure 3. Potential dependence of the logarithm of the heterogeneous rate constant for the reduction of DCP in DMF/0.1 M TBAP at $25\text{ }^{\circ}\text{C}$. The plot is formed from a collection of curves obtained at the Hg electrode in three separate experiments where ν was varied from 1 to 50 V s^{-1} .

the mid-potential of the range pertaining to the peak width (i.e. the potential at $3/4$ peak height), it turns out that $d\alpha/dE = 0.51\text{ V}^{-1}$.

The heterogeneous ET kinetics was therefore analyzed in a much more rigorous way by the convolution analysis,²⁸ which has the great advantage of allowing one to analyze the experimental voltammetric curves without the need of defining the ET rate law. Our typical procedure consisted of the digital acquisition of the background voltammetric curves, addition of the peroxide, new acquisition of curves under otherwise identical conditions, background subtraction, and convolution of the resulting curves.

The limiting convolution current, I_l , was found to be independent of the scan rate as expected on the basis of its definition, i.e. $I_l = nFAD^{1/2}C^*$,²⁸ where n is the overall electron consumption and D the diffusion coefficient. The diffusion coefficient was therefore readily calculated to be $4.7 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$, using a glassy carbon electrode of known area. Given the constancy of I_l , the convolution curves were then subjected to logarithmic analysis to obtain the potential dependence of the heterogeneous ET rate constant k , using the equation that holds for a completely irreversible process:²⁶

$$\ln k = \ln D^{1/2} - \ln \left(\frac{I_l - I(t)}{i(t)} \right) \quad (16)$$

which combines real and convoluted current values. A convolution curve derives from an integration procedure and therefore is rather insensitive to the noise affecting the original voltammetric curve; however, owing to the mixing of current data in eq 16, the real curve has to be acquired by using all of the possible expedients to reduce the noise to low levels (see Experimental Section) as otherwise the quality of the resulting $\ln k$ plots (and further elaborations) is greatly affected. The result of the logarithmic analysis is shown in Figure 3, where both the overall agreement between the sets of data pertaining to the different scan rates, obtained upon $1\text{ point}/\text{mV}$ acquisition, and the curvature of the plot can be noticed. By derivatization of the $(\ln k) - E$ plots, the apparent transfer coefficient α_{app} can be obtained according to the equation

$$\alpha_{\text{app}} = -\frac{RT}{F} \frac{d \ln k}{dE} \quad (17)$$

The equation is written in terms of the apparent value of the transfer coefficient because such a value is not yet corrected for the double layer. Derivatization was simply accomplished by linear regression of the experimental data within small E intervals (21 to 29 mV, depending on the quality of the $\ln k$ plots), therefore avoiding the temptation of treating directly the whole set of $(\ln k)-E$ plots according to a quadratic equation. The result of this procedure is shown in Figure 4. The plot is satisfactorily linear and the result of its regression analysis is given by the equation:

$$\alpha_{\text{app}} = 0.849 + 0.253E \quad (18)$$

Comparison of eqs 11, 15, and 17 shows that the real α coefficient is linked to α_{app} by

$$\alpha = 0.5 + \frac{F}{8\Delta G_0^\ddagger} (E - E^\circ - \phi^\ddagger) = \frac{\alpha_{\text{app}}}{1 - \partial\phi^\ddagger/\partial E} \quad (19)$$

and therefore α can be obtained once the function $\phi^\ddagger(E)$ is known. By using available data for the mercury electrode in DMF/0.1 M TBAP,³⁰ the α_{app} data were transformed into the corresponding α values, under the usual hypothesis that the reaction site can be identified with the outer Helmholtz plane,^{27b,33} leading to equation:

$$\alpha = 0.870 + 0.259E \quad (20)$$

Since $\alpha = 0.5$ when $E = E^\circ + \phi^\ddagger$, and considering that the diffuse layer potential is -0.11 V when $E \sim -1.3$ V,³⁰ use of eq 20 leads to the double-layer corrected estimate of the standard potential pertaining to step 12, i.e.

$$E^\circ_{(\text{PhMe}_2\text{CO})_2/\text{PhMe}_2\text{CO}\cdot, \text{PhMe}_2\text{CO}^-} = -1.32 \text{ V SCE} \quad (21)$$

a value that is remarkably close to the value of -1.29 V that was previously obtained by using thermochemical (BDFE) and electrochemical ($E^\circ_{\text{PhMe}_2\text{CO}^\cdot/\text{PhMe}_2\text{CO}^-}$) data.^{12b} Such a result is worth noting if one considers that the potential difference corresponds in energy terms to only 0.7 kcal/mol.

As a final remark, we should observe that the use of eq 18 would have led to a double-layer uncorrected estimate of -1.38 V, thanks to a partial compensation between the effects brought about by $\partial\phi^\ddagger/\partial E$, which tends to increase the slope of the α vs E plot compared to the α_{app} vs E plot and therefore to push the standard potential in the negative direction, and ϕ^\ddagger , which is negative and hence adjusts the potential to more positive values. Compared to the -1.29 V value, this would increase the difference to ca. 2 kcal/mol.

The reduction of DBP also takes place according to the two-electron stoichiometry given by eq 14,^{12a} where now $R = t\text{-Bu}$. As mentioned above, some experimental problems associated with the study of the reduction of DBP were caused by the fact that just prior to the solvent/electrolyte discharge the background subtraction procedure proved to be inaccurate. In fact, the background subtracted curves revealed a dip at very negative potentials, which led us to conclude that the electrolyte breakdown is somehow inhibited by the presence of the electroactive substrate. On the other hand, the potential region in which the background corrected data are unreliable is rather narrow being of the order of 0.1–0.15 V. The data of DBP

(33) Severin, M. G.; Arévalo, M. C.; Maran, F.; Vianello, E. *J. Phys. Chem.* **1993**, *97*, 150.

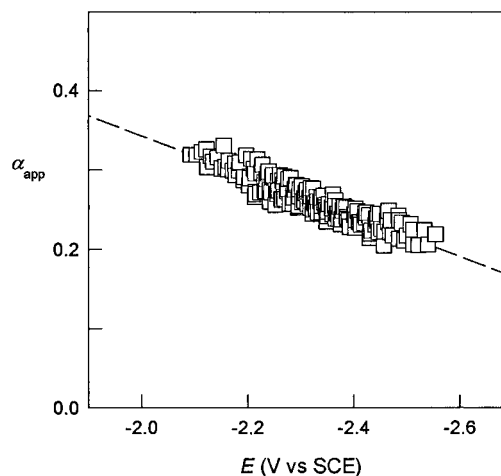


Figure 4. Potential dependence of the apparent transfer coefficient for the reduction of DCP in DMF/0.1 M TBAP at the Hg electrode. The dashed line derives from the linear regression analysis of the data. $T = 25$ °C.

were therefore treated in a different way that, though approximate, led to reasonable results. The experimental procedure was the same as above, the only difference being in the subsequent logarithmic analysis which required the knowledge of the limiting convolution current I_l . Since I_l can be determined for most of the scan rates only in the potential region affected by the dip, we resorted to analyze the rising part of the convolution curves according to a nonlinear sigmoidal fit that led to the expected I_l value for each scan rate.³⁴ The result was rather satisfactory in that the I_l values were very close to each other, almost within the 2% maximum difference that we usually find for such limiting currents. Therefore, we proceeded in the analysis, along similar lines as described above for DCP, to obtain the following electrochemical estimate for the double-layer corrected standard potential

$$E^\circ_{(t\text{-BuO})_2/t\text{-BuO}\cdot, t\text{-BuO}^-} = -1.62 \text{ V SCE} \quad (22)$$

a value which, though obviously approximate, is not too far from the completely thermochemical estimate of -1.44 V.^{12a,35}

The results obtained with the above peroxides, in particular DCP, the data of which were treated under the most favorable conditions, led us to extend the same type of analysis to the heterogeneous reduction of three compounds (DTP, BTP, CTP) of unknown BDFE and characterized by having a common moiety, Ph_3CO^- , and being reducible at not very negative potentials, i.e. in a more convenient region. The voltammetric curves, which for the three compounds were always of very good quality in the 0.2–20 V s^{-1} range (up to 100 V s^{-1} for DTP), were analyzed by convolution to yield the α_{app} vs E plots,

(34) The $I-E$ curves are typical sigmoidal transition curves.²⁸ Our best convolution data, obtained in the 0.2–2 V s^{-1} range, were treated according to equation

$$I(E) = a_0 + \frac{a_1}{1 + \exp[-(E - a_2)/a_3]}$$

in which a_0 , a_1 , a_2 , and a_3 are constants.

(35) In our previous work (ref 12a) the standard potential was estimated by using the BDFE for decomposition of the neat peroxide. Whereas the BDE of DBP is believed to be solvent independent based on photoacoustic calorimetric studies (Wayner, D. D. M.; Luszyk, E.; Pagé, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J.; Aldrich, H. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737), it is not clear that this should be so with the entropy change associated with homolysis. Since the standard potential in eq 22 leads to a BDFE value of 32 kcal/mol (viz. 28 kcal/mol from ref 12a) in DMF, we can estimate an entropy contribution to homolysis ($-\Delta S$) of 6 kcal/mol in this solvent.

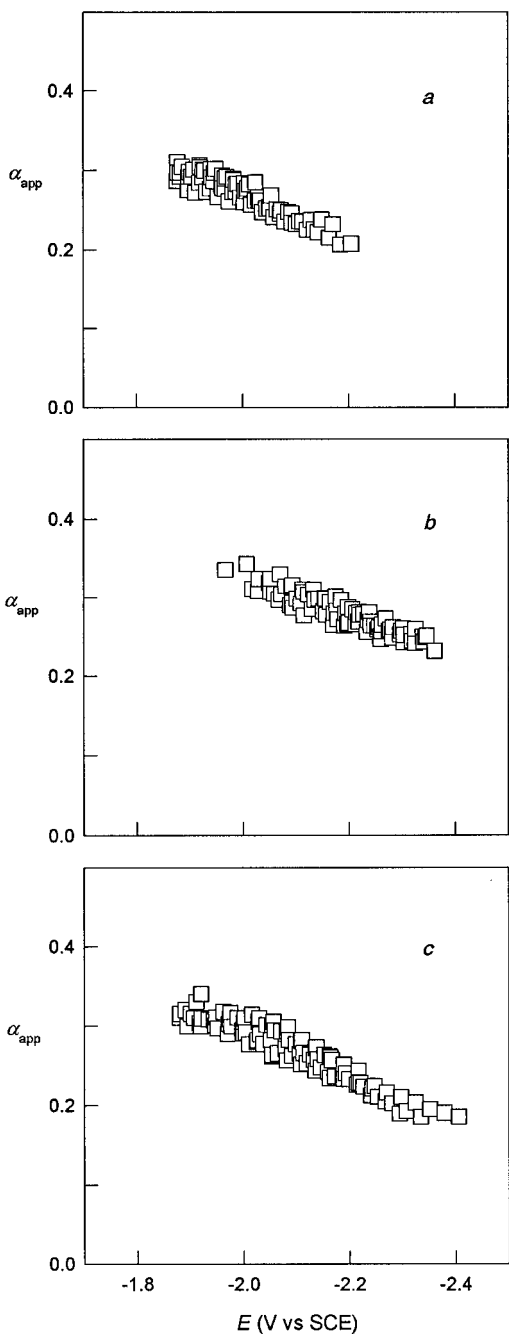


Figure 5. Potential dependence of the apparent transfer coefficient for the reduction of DTP (plot a), BTP (plot b), and CTP (plot c) in DMF/0.1 M TBAP at the Hg electrode. $T = 25\text{ }^{\circ}\text{C}$.

depicted in Figure 5. After correction for the double layer, the following dissociative ET standard potentials were estimated:

$$E^{\circ}_{(\text{Ph}_3\text{CO})_2/\text{Ph}_3\text{CO}^{\bullet}, \text{Ph}_3\text{CO}^-} = -1.13\text{ V SCE} \quad (23)$$

$$E^{\circ}_{t\text{-BuOOCPh}_2/t\text{-BuO}^{\bullet}, \text{Ph}_3\text{CO}^-} = -1.22\text{ V SCE} \quad (24)$$

$$E^{\circ}_{\text{PhMe}_2\text{COOCPh}_2/\text{PhMe}_2\text{CO}^{\bullet}, \text{Ph}_3\text{CO}^-} = -1.15\text{ V SCE} \quad (25)$$

Assuming that we have corrected properly for the double-layer effect, which is sustained by the self consistency of the results concerning DCP, we can estimate that the experimental error associated to such E° estimates is probably within $\pm 0.05\text{ V}$.

The best way to check the reliability of such double-layer corrected E° s is to make use of eq 10, which relates the dissociative ET standard potentials to other quantities, thanks

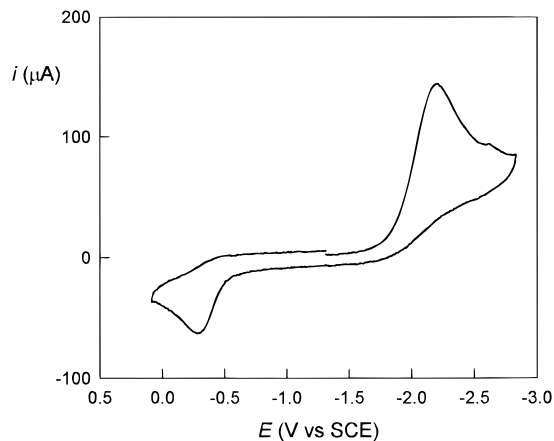


Figure 6. Cyclic voltammetry for the reduction of 2.89 mM CTP in DMF/0.1 M TBAP at the GC electrode. $T = 25\text{ }^{\circ}\text{C}$, $\nu = 1\text{ V s}^{-1}$.

to the thermochemical cycle 7–9. The standard potential for the alkoxy radical/alkoxide ion couple, $E^{\circ}_{\text{Ph}_3\text{CO}^{\bullet}/\text{Ph}_3\text{CO}^-}$, was obtained by cyclic voltammetry measurements. The experiments were carried out with use of a glassy carbon electrode by scanning the potential initially toward negative values, to include the reduction peak of the selected peroxide, and then extending the backward scan to rather positive potentials, typically +0.1 V. In this way it is possible to detect the anion that is electrogenerated during the direct scan, as shown by the cyclic voltammogram reported in Figure 6. The best data were obtained with CTP, though very similar results were also obtained with DTP and BTP. Concerning the nature of the species undergoing the oxidation, it should be observed that the two-electron reduction in the forward scan produces both anionic fragments so that both oxidations might be observed in the reverse scan. On the other hand, the basicity of the anion plays a key role in the detection of the peak: whereas $t\text{-BuO}^-$ is too basic to survive in appreciable amounts in a medium that contains water traces, the basicity of PhMe_2CO^- and that of Ph_3CO^- are such to allow the observation of the peak.³⁶ Moreover, whereas ν must be higher than 0.5 V s^{-1} in the first case,¹² the oxidation peak can be seen with Ph_3CO^- even at scan rates as low as 0.05 V s^{-1} . The consequence is that the oxidation peak observed at low scan rates with CTP is essentially due only to the oxidation of Ph_3CO^- .

The oxidation peak is located at -0.308 V at 0.2 V s^{-1} and is irreversible, and the peak potential shifts by $28.4\text{ mV}/\log \nu$ in the $0.1\text{--}1\text{ V s}^{-1}$ range, though the shift becomes larger at higher scan. The peak potential shift is in good agreement with a first-order reaction,²⁷ causing the disappearance of the electrogenerated $\text{Ph}_3\text{CO}^{\bullet}$ radical, a species the lifetime of which can be estimated to be ca. 10 ps .³⁷ Given such kinetic information, the standard potential for the radical/anion couple is easily obtained from good experimental E_p values.²⁷ The average of the results obtained with CTP is -0.030 V , a value that will be used subsequently; nevertheless, it should be

(36) (a) Whereas the $\text{p}K_a(\text{DMF})$ of $t\text{-BuOH}$ and that of water can be calculated to be 32.5 and 31.7, respectively,^{36b} the $\text{p}K_a$'s of PhMe_2OH and Ph_3OH do not seem to be known; however, taking into account the acidity scale of alcohols^{36c} and substituent effects, it is reasonable to assume that their $\text{p}K_a$ values are about 2–3 units smaller than that of water. (b) The $\text{p}K_a(\text{DMF})$ values can be obtained from the corresponding DMSO data^{36c} by using the correlation $\text{p}K_a(\text{DMF}) = 1.56 + 0.96\text{ p}K_a(\text{DMSO})$: Maran, F.; Celadon, D.; Severin, M. G.; Vianello, E. *J. Am. Chem. Soc.* **1991**, *113*, 9320. (c) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295.

(37) (a) Falvey, D. E.; Khanbatta, B. S.; Schuster, G. B. *J. Phys. Chem.* **1990**, *94*, 1056. (b) See, also: Avila, D. V.; Ingold, K. U.; Di Nardo, A. A.; Zerbetto, F.; Zgierski, M. Z.; Luszyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 2711.

Table 2. Calculated and Experimental Parameters for the Reduction of Dialkyl Peroxides in DMF/0.1 M TBAP and $T = 25^\circ\text{C}$

substrate	DBP	DCP	DTP	BTP	CTP
$E^\circ_{\text{AB/A}^+\cdot\text{B}^-}$ (V)	-1.44 ^a -1.62	-1.32	-1.13	-1.22	-1.15
$E^\circ_{\text{B}^+\cdot\text{B}^-}$ (V)	-0.23 ^a	-0.12 ^b	-0.03	-0.03	-0.03
BDFE (kcal/mol)	28 ^a 32 ^c	27.7	25.4	27.4	25.8
$r_{\text{effective}}$ (Å)	3.35 ^d	3.53	4.34	3.92	3.87
$\lambda_o^{\text{(Marcus)}}$ (kcal/mol)	11.5	10.9	8.9	9.8	9.9
$\lambda_o^{\text{(Hush)}}$ (kcal/mol)	23.0	21.8	17.8	19.6	19.8
$\lambda_o^{\text{(K-B)}}$ (kcal/mol)	16.6	15.8	12.9	14.2	14.4
λ' (kcal/mol)	15.9 ^g	10.8	8.2	12.8	9.8

^a From ref 12a. ^b From ref 12b. ^c Obtained by convolution analysis. ^d From the density of the compound; see ref 40b. ^e From selected Kojima-Bard data,^{40b} using eq 27. ^f This work. ^g Using the convolution BDFE.

mentioned that the more qualitative analysis carried out on BTP and DTP led to -0.036 and -0.040 V, respectively.

The determination of $E^\circ_{\text{Ph}_3\text{CO}^+/\text{Ph}_3\text{CO}^-}$ is important because this potential is to be used in eq 10, together with the standard potentials obtained by convolution analysis of the reduction data of DTP, BTP, and CTP; besides DTP, for which the formation of Ph_3CO^- in the dissociative ET is obvious, it is in fact very likely, on the basis of simple substituent effects, that the initially formed anionic fragment is Ph_3CO^- also in the case of BTP and CTP. Accordingly, the BDFE values pertaining to these peroxides can be easily calculated and are reported in Table 2. It is worth noting that the calculated values are very similar, almost equal within experimental error. Since the entropy term is not expected to be very different in the investigated series,³⁵ the similarity of the BDFE values (including those of DCP and DBP) reflects what is known about the small substituent effect on the BDEs of such compounds.³⁸ The double-layer corrected convolution approach seems therefore to work rather satisfactorily for such compounds.

The self-consistency of the data can be used to perform some other calculations that are related to a problem that arises when experimental ET data are to be compared with theoretical ones, i.e. the evaluation of the reorganization energy λ . This is particularly true in the heterogeneous case owing to the fact that the solvent reorganization term may be calculated in different ways. To calculate the solvent reorganization energy for the investigated peroxides the following procedure was adopted. The Stokes radii of the starting molecules were calculated starting from the experimental diffusion coefficients through the Stokes-Einstein equation. The radii were then transformed into the corresponding effective radii (Table 2), following the concept that the incipient negative charge, owing

(38) (a) Baldwin, A. C. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; p 97. (b) Ando, W., Ed. *Organic Peroxides*; Wiley: New York, 1992. (c) Bach, R. D.; Ayala, P. Y.; Schlegel, H. B. *J. Am. Chem. Soc.* **1996**, *118*, 12758.

(39) (a) See for example ref 4b and: Peover, M. E.; Powell, J. S. *J. Electroanal. Chem.* **1969**, *20*, 427. (b) The effective radii were calculated by using the equation

$$r = \frac{r_{\text{B}}(2r_{\text{AB}} - r_{\text{B}})}{r_{\text{AB}}}$$

where AB is the starting molecule and B the ionic fragment. Such an equation was initially used for the dissociative ET to halides^{8,13} and then to peroxides.¹² Whereas halide-ion solvation is symmetrical, in the case of alkoxide ions the negative charge, being concentrated onto the oxygen atom, is not expected to cause significant reorganization of the solvent molecules around the bulky hydrocarbon side of the ion itself. Therefore, an effective radius for the alkoxides was calculated by using once again the above equation, where now AB is the alkoxide and B the oxygen atom.

to the breaking O-O bond, is going to develop in only half of the starting peroxide and therefore that some screening to the solvent reorganization is brought about by the second, uncharged molecular fragment.³⁹ Analogous reasoning was applied to the calculation of the radius of the leaving alkoxide ion. The solvent reorganization energy was then calculated from such effective radii, using both the Marcus and Hush approach,^{40a} i.e. by the equation

$$\lambda_o = e^2 \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right) \frac{1}{nr} \quad (26)$$

where $n = 4$ (Marcus) or 2 (Hush), e is the charge of the electron, and ϵ_{op} and ϵ_s are the high-frequency and static dielectric constants of the solvent, respectively. The solvent reorganization energy was also calculated by using a rough correlation which derives from several data pertaining to the heterogeneous reduction of aromatic compounds,^{40b} i.e.

$$\lambda_o = 55.7 \frac{1}{r} \quad (27)$$

where λ_o is given in kcal/mol and r in Å. This approach was previously adopted and preferred to analyze the reduction of various substrates.^{4b,8,12} The result of the three different calculations is given in Table 2. We used both the experimental activation-driving force relationships and the E° determinations to obtain an evaluation of λ . The slope of the regression analysis of the α vs E plots, γ , is in fact directly linked (see eq 6) to the intrinsic barrier through the equation

$$\Delta G_o^\ddagger = \frac{F}{8\gamma} \quad (28)$$

The BDFEs obtained as described above can be transformed into BDEs, using a common entropy contribution of $T\Delta S = 6$ kcal/mol³⁵ and thus allowing estimates of λ by using eq 5. The values pertaining to the five peroxides are given in Table 2. Comparison of the theoretical (eq 26) and empirical (eq 27) data with the experimental estimates reveals that the latter values are generally between the empirical and the Marcus predictions. In general, while it is possible to determine the free energy changes associated with a dissociative process with reasonable accuracy, extracting the solvent reorganization energies still represents a significant challenge. Our results, based on very careful electrochemical measurements with convolution analysis, provide heterogeneous kinetic data of unusually high quality over a large potential range and provide convincing verification of the Savéant theory of dissociative electron transfer. Consequently, we expect that this experimental approach will ultimately provide better understanding of the reorganization energies associated with electrode processes.

Conclusions

The possibility of studying the heterogeneous ET to dialkyl peroxides at the mercury electrode has provided the opportunity to test the dissociative ET theory by using experimental activation-driving force relationships. The convolution voltammetry approach coupled to the double-layer correction proved to be a remarkably powerful tool in evaluating the standard potential for the dissociative ET to dialkyl peroxides, as supported, whenever possible, by comparison with independent estimates of the E° values.

(40) (a) See ref 43b and pertinent references cited therein. (b) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317.

The use of the thermodynamical cycle 7–9 and therefore of eq 10 that allows one to estimate BDFEs from the above E° s together with the standard potential for the B^*/B^- couple is also worth noting. In fact, in favorable conditions, the latter quantity can be determined through analysis of the voltammetric oxidation of the B^- anion. In this way, reasonable estimates of solution BDFEs were obtained for some dialkyl peroxides.

In treating the heterogeneous data, the double-layer effect has to be taken into account. However, our results showed that the difference between the E° calculations carried out by using either α or α_{app} amounts to only 0.06–0.07 V. It appears therefore that provided the potential is not more positive than, say, -1 V, i.e. under the conditions in which the relative compensation between the ϕ^\ddagger and $\partial\phi^\ddagger/\partial E$ effects still holds, the use of the experimental α_{app} may lead to a fairly good estimate of the double-layer corrected E° ; this fact is particularly important if it could be extended to good experimental data

obtained with electrode materials, the double-layer properties of which are unknown.

Finally, the approach of combining the E° estimate, through eq 10, with the curvature of the activation–driving force relationship (eq 6) seems to be promising in finding new guidelines to estimate the heterogeneous ET reorganization energies.

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Supporting Information Available: Details of the preparation of mercury electrodes (3 pages). See any current masthead page for ordering and Internet access instructions.

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