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Reduction of Di-*tert*-Butyl Peroxide: Evidence for Nonadiabatic Dissociative Electron Transfer[1a]

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Electron transfer to organic molecules (A−B) is often accompanied by bond cleavage with the formation of a radical, A•, and an anion, B⁻. This process can occur by a stepwise mechanism, with the intermediacy of a radical anion AB•⁻ (eqs 1 and 2), or occur in a single elementary step (eq 3). The latter

$$A{-}B + e^- \rightleftarrows A{-}B^{\bullet -} \tag{1}$$

$$A{-}B^{\bullet -} \rightarrow A^\bullet + B^- \tag{2}$$

$$A{-}B + e^- \rightarrow A^\bullet + B^- \tag{3}$$

process, in which electron transfer and bond cleavage are concerted, is usually referred to as a dissociative electron transfer.[2] A valuable contribution to understanding this process has been made by Savéant, who developed a theory for adiabatic dissociative electron transfer[3] in which the activation energy−driving force relationship (eq 4) is a Marcus-like quadratic equation, where ΔG° is the standard free energy of the reaction and $\Delta G_0^\ddagger$ is the free energy of activation at zero driving force. For a dissociative electron transfer, $\Delta G_0^\ddagger$ includes a term for the bond dissociation free energy (BDFE) of the A−B bond in addition to the usual reorganization term, λ_o (eq 5).

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

$$\Delta G_0^\ddagger = (\lambda_o + \mathrm{BDFE})/4 \tag{5}$$

To test the Savéant theory, reliable thermochemical data are required for the homolysis of the A−B bonds for the determination of $\Delta G_0^\ddagger$. Thus, good support for the model has been found with alkyl halides, where the relevant BDFE values are available.[2,4] However, given the paucity of reliable thermochemical data for A−B homolysis, the extension of the Savéant theory to systems more complex than organic halides is still to be verified. One class of compounds for which the thermochemistry is well established and which are expected to undergo dissociative electron tranfer is organic peroxides (ROOR). Consequently, we have begun a detailed investigation of the reduction of these species. We now report preliminary results obtained with di-*tert*-butyl peroxide (DTBP) upon both direct electroreduction and homogeneous electron transfer from electrogenerated radical anions. From the analysis of the data it is clear that the reduction of DTBP is not adequately described by Savéant's theory, and we conclude that this is the first example of a nonadiabatic dissociative electron transfer.

The reduction of DTBP by cyclic voltammetry in *N,N*-dimethylformamide (DMF) is irreversible with a peak at −2.50 V vs SCE (0.2 V s^{-1}) and has the following characteristics:[5] (a) the position and shape are unaffected by addition of acids stronger than *t*-BuOH (*e.g.*, fluorene or acetanilide); (b) the peak potential E_p shifts negatively by 128 mV upon 10-fold increase of the scan rate, providing a value of 0.231 for the transfer coefficient, α;[6] and (c) the peak width (*i.e.*, the difference between the value of the potential at half-peak height and E_p) depends on the scan rate and leads to values for α of 0.254 and 0.235 at 0.2 V s^{-1} and 2 V s^{-1}, respectively, suggesting a potential dependence of α. The rate constants for heterogeneous electron transfer, k_{HET}, were determined as a function of potential by convolution analysis[7] of the voltammetric curves obtained between 0.1 and 2 V s^{-1}. A plot of $\log\{k_{\mathrm{HET}}(E)\}$ *vs* E led to a potential dependence for the apparent α of 0.21 V^{-1}. Extrapolation to α = 0.5 provided an estimate of the standard potential for the reduction of DTBP[8] of −1.25 V vs SCE. Controlled potential electrolysis of DTBP leads to the consumption of 2 F mol^{-1} in both DMF and acetonitrile (MeCN).[5] Overall, the voltammetric analysis indicated that DTBP was reduced irreversibly with an overpotential of ca. 1.2 V, according to the overall stoichiometry indicated by eq 6.

$$t\text{-BuOOBu-}t + 2e^- \rightarrow 2\ t\text{-BuO}^- \tag{6}$$

The standard potential for the dissociative reduction of DTBP ($E^\circ_{t\text{-BuOOBu-}t/t\text{-BuO}^\bullet,t\text{-BuO}^-}$) can be calculated from a thermochemical cycle[9] (eq 7). The BDFE of DTBP is estimated to be 28 ± 2 kcal mol^{-1} [10,11] and the $E^\circ_{t\text{-BuO}^\bullet/t\text{-BuO}^-}$ calculated to be −0.23 and −0.30 V vs SCE in DMF and MeCN, respectively.[10,11] This leads to values for $E^\circ_{t\text{-BuOOBu-}t/t\text{-BuO}^\bullet,t\text{-BuO}^-}$ of −1.44 and −1.51 V vs SCE in DMF and MeCN, respectively, in reasonable agreement with the electrochemical estimate.

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[2] See, for example: Savéant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455 and references cited therein.

[3] (a) Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788. (b) Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 10595.

[4] (a) Huang, Y.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1994**, *116*, 2157. (b) Clark, K. B.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1991**, *113*, 9363.

[5] Voltammetric experiments were run at 25° C under argon atmosphere in the appropriate solvent containing 0.1 M tetraethylammonium perchlorate using glassy carbon (Tokai GC-20) as the electrode material. Ferrocene was used as the internal redox reference, and the potential was then calibrated against the KCl saturated calomel electrode (SCE). Under our conditions, $E^\circ_{\mathrm{Fc^+/Fc}}$ is 0.475 and 0.450 V *vs* SCE in DMF and MeCN, respectively. Electrolyses were carried out in a divided cell at a Hg pool cathode both in the presence (1.93 F mol^{-1} (DMF); 2.00 F mol^{-1} (MeCN)) and in the absence of acetanilide (1.88 F mol^{-1} (DMF)). Conventional electrochemical instrumentation (EG&G-PARC) was employed.

[6] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; Wiley: New York, 1980.

[7] (a) Savéant, J.-M.; Tessier, D. *J. Electroanal. Chem.* **1975**, *65*, 57. (b) Savéant, J.-M.; Tessier, D. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 57 and references cited therein.

[8] This holds independently of the dissociative (ref 3) or outer-sphere character of the electron transfer: (a) Savéant, J.-M. *Adv. Phys. Org. Chem.* **1990**, *26*, 1. (b) Marcus, R. A. In *Special Topics in Electrochemistry*; Rock, P. A., Ed.; Elsevier: New York, 1977. (c) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

[9] Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287.

[10] The BDFE of DTBP was estimated to be 28 ± 2 kcal mol^{-1} (1.21 ± 0.08 eV). From the gas phase bond dissociation enthalpy (38 kcal/mol) corrected for the entropy (36 cal mol^{-1} K^{-1}) (ref 11a) is obtained a value of 27.3 kcal mol^{-1}. On the other hand, estimating the K_{eq} for the homolysis of DTBP from kinetic data in solution (ref 11b) leads to a value of 28.7 kcal mol^{-1}. The value of $E^\circ_{t\text{-BuO}^\bullet/t\text{-BuO}^-}$ was calculated for both DMF and MeCN from $E^\circ_{t\text{-BuO}^\bullet/t\text{-BuO}^-} = \mathrm{BDFE}_{t\text{-BuOH}}/F - 2.3(RT/F)\mathrm{p}K_a + E^\circ_{\mathrm{H^-/H^\bullet}}$. The BDFE of *t*-BuOH for the two solvents was obtained from literature data (ref 11a) and corrected for solvation of H• (ref 9). The pK_a values for *t*-BuOH were obtained by transforming the DMSO value, 32.2 (ref 11c), into the corresponding DMF and MeCN values, *i.e.*, 32.5 and 44.8, respectively (from pK_a(DMF) = 1.56 + 0.96 pK_a(DMSO), ref 11d; and pK_a(MeCN) = 7.1 + 1.17 pK_a(DMSO), using data for O−H acids from ref 11e).

[11] (a) NIST Standard Reference Database 25. *NIST Structures and Properties Database and Estimation Program*, 1991; U.S. Department of Commerce: Gaithersburg, MD 20899, 1991. (b) Matsugo, S.; Saito, I. In *Organic Peroxides*; Ando, W., Ed.; Wiley,: New York, 1992. (c) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295. (d) Maran, F.; Celadon, D.; Severin, M. G.; Vianello, E. *J. Am. Chem. Soc.* **1991**, *113*, 9320. (e) Izutzu, K. *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents*; Chemical Data Series No. 35; Blackwell Scientific Publications: Oxford, 1990.

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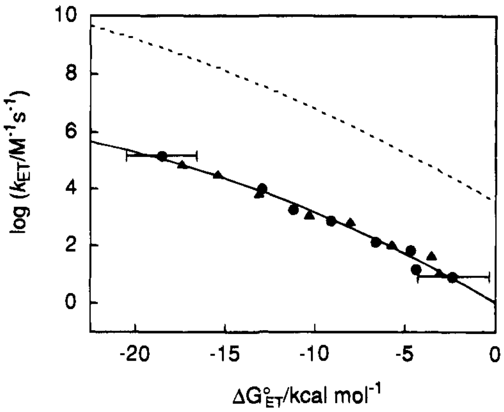

Figure 1. Plot showing the variation in the logarithm of the rate constant of electron transfer, log(k_{ET}), with the driving force, $\Delta G^\circ_{ET} = -F(E^\circ_{t\text{-BuOOBu-}t/t\text{-BuO}^\bullet,t\text{-BuO}^-} - E^\circ_{\text{ArH/ArH}^{\bullet-}})$, for the homogeneous electron transfer reactions of a number of aromatic radical anions with DTBP in DMF (●) and acetonitrile (▲). The error bars shown represent an estimate in the uncertainty in the driving force and will be the same for all data points. The solid line is that obtained by nonlinear least squares fitting of the data to eq 4. The dashed line is that predicted on the basis of Savéant's theory (see text).

$$E^\circ_{t\text{-BuOOBu-}t/t\text{-BuO}^\bullet,t\text{-BuO}^-} = E^\circ_{t\text{-BuO}^\bullet/t\text{-BuO}^-} - \frac{\text{BDFE}}{F} \quad (7)$$

The homogeneous electron transfer was studied using a series of aromatic radical anions ($\text{ArH}^{\bullet-}$) as outer-sphere electron transfer donors (eq 8), using the method of homogeneous redox catalysis.[12,13] The radical anions were generated by voltammetry in the absence and then in the presence of varying amounts of DTBP. The current increase, resulting from an overall two-electron process (eq 6), provides a measure of the catalytic efficiency. Comparison of the data with relevant theoretical curves and analysis by digital simulation led to values for the rate constant for homogeneous dissociative electron transfer, k_{ET}.

$$\text{ArH}^{\bullet-} + t\text{-BuOOBu-}t \xrightarrow{k_{ET}} \text{ArH} + t\text{-BuO}^\bullet + t\text{-BuO}^- \quad (8)$$

A plot of log(k_{ET}) vs ΔG°_{ET} is shown in Figure 1. The data shown are for experiments performed in both DMF and MeCN and are averages of the values obtained in both laboratories. The error bars are estimates of the uncertainty in ΔG° based mainly on the uncertainty in $E^\circ_{t\text{-BuOOBu-}t/t\text{-BuO}^\bullet,t\text{-BuO}^-}$. The figure also shows the theoretical prediction based on Savéant's theory of adiabatic dissociative electron transfer (eqs 4 and 5) in which the BDFE is 28 kcal mol^{-1} and λ_o is estimated to be 15 kcal mol^{-1}.[14,15] The surprising observation is that the experimental values are *3.5–4 orders of magnitude smaller* than the values predicted by the Savéant theory.

There are a number of possible explanations for the discrepancy between the experimental results and the theory. First, there may be errors in the thermochemical data. A difference of 3.5 orders of magnitude would correspond to an underestimate of *ca.* 19 kcal mol^{-1} in λ_o or 7 kcal mol^{-1} in the BDFE of DTBP (since the BDFE is used to determine both ΔG° and $\Delta G_0^\ddagger$). While the error in the BDFE of DTBP will not exceed ±2 kcal mol^{-1}, the error in λ_o may be as much as ±4 kcal mol^{-1}.[14] A second possibility is that the electron transfer is sterically inhibited (since the O–O bond is shielded by the *tert*-butyl groups), resulting in a reduction in k_{ET} due to the exponential decrease of the electronic coupling between the reactant and product states, H_{rp} (as observed with other systems[16]). However, if one assumes that the encounter distance is the sum of the van der Waals radii of the molecules, then a decrease of no more than 1.5 orders of magnitude in k_{ET} is expected.

Thus, even by consideration of the steric inhibition to electron transfer the experimental points remain at least 2 orders of magnitude below the theoretical curve, suggesting that in addition to being inhibited by steric constraints the electron transfer is nonadiabatic (*i.e.*, the electronic coupling energy, H_{rp}, is <50 cm^{-1}).[17,18] To our knowledge, this would represent the first example of a nonadiabatic dissociative electron transfer. The results may have implications on the generality of the Savéant theory as a tool for determining BDFE of A–B bonds in solution. While it has been demonstrated that this approach is, indeed, useful for the analysis of organic halides,[2] caution should be exercised when extending it to other systems, especially those containing weak σ-bonds. This problem, together with the study of less hindered peroxides, is currently under active investigation in our laboratories.

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[12] The following aromatics were used as redox mediators (standard potential V *vs* SCE in DMF): chrysene (−2.245); 7,8-benzoquinoline (−2.150); pyrene (−2.004); anthracene (−1.928); 9,10-diphenylanthracene (−1.837); fluoranthene (−1.729); perylene (−1.645); acenaphthylene (−1.633); naphthacene (−1.545).

[13] (a) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant J.-M. *J. Electroanal. Chem.* **1980**, *113*, 19. (b) Andrieux, C. P.; Savéant J.-M. *J. Electroanal. Chem.* **1986**, *205*, 43.

[14] The value of λ_o was estimated from the experimentally determined relationship with the molecular radius (ref 15a) using the method described by Savéant to calculate the effective radius of molecules undergoing dissociative electron transfer (refs 3b, 15b). The predicted rate constant was calculated from the Eyring equation in which the preexponential term was 3 × 10^{11} s^{-1} (ref 15a).

[15] (a) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317. (b) Andrieux, C. P.; Le Gorande, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892.

[16] See, for example: Sutin, N. In *Electron Transfer in Inorganic, Organic, and Biological Systems*; Bolton, J. R., Mataga, N., McLendon, G., Eds.; Advances in Chemistry Series 228; American Chemical Society: Washington, DC, 1991.

[17] If one assumes that the classical expression for the rate constant of an outer-sphere nonadiabatic electron transfer (refs 8b, 18) and that an exponential dependence of H_{rp} on the separation distance, r (ref 16), can be applied for the case of dissociative electron transfer, then a value of H_{rp}° (*i.e.*, the value of H_{rp} at $r = r_0$, where r_0 is the contact separation of the interacting orbitals) of only 11 cm^{-1} is obtained. This value is derived assuming that, at the actual reaction distance, $r - r_0 = 3$ Å and the attenuation factor for the distance dependence is the usual value of 1 Å^{-1}.

[18] (a) Marcus, R. A.; Sutin, N. *Biochem. Biophys. Acta* **1985**, *811*, 265. (b) German, E. D.; Kuznetzov, A. M. *J. Phys. Chem.* **1994**, *98*, 6120.