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Solvent Reorganization as a Governing Factor in the Kinetics of Intramolecular Dissociative Electron Transfers. Cleavage of Anion Radicals of α-Substituted Acetophenones

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Cleavage of ion radicals[2−6] may be viewed as an intramolecular electron transfer coupled with bond breaking in cases where the unpaired electron initially resides in an orbital that does not belong to the leaving group:[7]

$$^{-\bullet}R{-}X \rightleftharpoons R^{\bullet} + X^{-}$$

The unpaired electron jumps from the initial orbital to the σ^* orbital of the R−X bond which breaks simultaneously. Hence, a model of the dynamics of such reactions has been proposed[8] where the two main reaction coordinates are the bond distance and a fictitious charge representing solvent reorganization in the Marcus way.[9] The activation free energy, $\Delta G^{\ddagger}$, is thus related quadratically to the standard free energy of the reaction, ΔG°:

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}(1 + \Delta G^\circ/4\Delta G_0^{\ddagger})^2 \qquad (1)$$

The standard free energy of activation, $\Delta G_0^{\ddagger}$, is the sum of two contributions, one related to bond breaking and the other to solvent reorganization:

$$\Delta G_0^{\ddagger} = \frac{D_{RX^{\bullet-}} + \lambda^\circ}{4} \qquad (2)$$

where the first term may be derived from accessible molecular parameters according to

$$D_{RX^{\bullet-}} = D_{RX} + E^\circ_{RX/RX^{\bullet-}} - E^\circ_{R^\bullet/R^-} + T(S_{R^\bullet} - S_{RX}) + T(S_{RX^{\bullet-}} - S_{R^-}) \qquad (3)$$

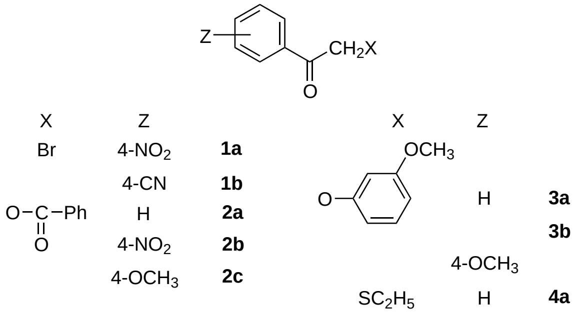
(the D, E°, and S values are the bond dissociation energies, the standard potentials, and the molar entropies of the subscript species, respectively). The solvent reorganization energy arises from the fact that, during the reaction, the charge moves from one portion of the molecule to another. λ° may thus be estimated from

$$\lambda^\circ = e_0^{\,2}\left(\frac{1}{2a_{RX^{\bullet-}}} + \frac{1}{2a_{R^\bullet,X^-}} - \frac{1}{d}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \qquad (4)$$

$a_{RX^{\bullet-}}$ is the radius of the sphere approximating the region of the starting anion radical where the charge is initially located and $a_{R^\bullet,X^-}$, the radius of the sphere approximating the location of the charge on the leaving group when the bond is broken. d is the distance between the centers of charge at the transition state. The D values are the optical and static dielectric constants, respectively. The standard free energy of anion radical cleavage may be obtained from eq 5, where ΔS_{RX} is the entropy for the cleavage of R−X.

$$\Delta G^\circ = D_{RX} + E^\circ_{RX/RX^{\bullet-}} - E^\circ_{X^\bullet/X^-} - T\Delta S_{RX} \qquad (5)$$

So far, only the influence of the intramolecular factors (through eqs 1−3) have been investigated experimentally (see refs 6d and 8) in reactions where they are largely predominant over possible solvent reorganization effects.[10] In order to maximize the effect of solvent reorganization and minimize the contribution of intramolecular factors, we have selected a series of anion radicals generated by electrochemical reduction of the following α-substituted acetophenones.



Over the whole series of anion radicals generated by cyclic voltammetry, only **2b**$^{\bullet-}$ was found to be stable down to the lowest scan rate (0.1 V/s).[11] **4a** exhibts an irreversible wave at low scan rate which becomes reversible around 10 V/s. The cleavage rate constant and the standard potential for the formation of the anion radical of **4a** were derived from these cyclic voltammetric data (see the supporting information). All the other compounds give rise to an irreversible wave between

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(7) In the opposite case,[7b−j] the reaction is better viewed as a homolysis and the intramolecular (small) reorganization pertains essentially to rehybridization.[7b] The solvent reorganization energy is also expected to be small since the charge stays on the same portion of the molecule during bond cleavage. (b) Anne, A.; Fraoua, S.; Moiroux, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1996**, *118*, 3938. (c) Maslak, P.; Vallombroso, T. M.; Chapman, W. H.; Narvaez, J. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 73. (d) Maslak, P.; Narvaez, J. N.; Vallombroso, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12373. (e) Maslak, P.; Chapman, W. H.; Vallombroso, T. M.; Watson, B. A. *J. Am. Chem. Soc.* **1995**, *117*, 12380.

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(11) It is interesting to note that charge transfer to **2b** is relatively slow. The standard rate constant, $k_S = 0.22$ cm^{-1} s^{-1}, was determined from cyclic voltammograms (see the supporting information). Charge transfer to acetophenone itself is even slower ($k_S = 0.14$ cm^{-1} s^{-1}), pointing to a strong localization of the negative charge on the carbonyl oxygen of the anion radical in both cases, albeit somewhat less with **2b** than with acetophenone.

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Table 1. Reactivity Data[a]

							contributions	
cmpd	log k (s^{-1})	D_{RX}[b]	$E°_{X^\bullet/X^-}$	$-E°_{RX/RX^{\bullet-}}$	$-\Delta G°$[j] (cleav)	$\Delta G_0^{\ddagger}$[k]	intra[l]	solv[m]
1a	6.6	1.85[c]	1.44[e]	0.83	0.71	0.65	0.26	0.39
1b	7.8	1.90[c]	1.44[e]	1.04	0.87	0.66	0.22	0.44
2a	6.4	2.53[d]	1.24[f,g]	1.81	0.82	0.72	0.18	0.54
2c	7.6	2.53[d]	1.24[f,g]	1.97	0.98	0.7	0.14	0.56
3a	5.4	1.78[d]	0.24[f,h]	1.81	0.56	0.68	0.00	0.68
3b	5.4	1.78[d]	0.24[f,h]	1.88	0.63	0.69	0.00	0.69
4a	1.2	2.14[d]	0.06[f,i]	1.87	0.08	0.71	0.07	0.64

[a] Energies in eV, potentials in V vs SCE. [b] From the value $D_{RX} = 2.05$ eV obtained from the peak potential, E_p, of the dissociative electron transfer reduction of $PhCOCH_2Br$ by means of the equation: $D_{RX} = (2/3)(E°_{X^\bullet/X^-} - E_p)$[14a,b] (details on the electrochemistry of $PhCOCH_2Br$ will be published elsewhere). [c] The value for $PhCOCH_2Br$ is corrected for the weakening of the bond by the para electron-withdrawing substituent as for the corresponding benzyl bromides.[14a,c] [d] From $D_{PhCOCH_2X} = D_{PhCOCH_2Br} + D_{PhCH_2X} - D_{PhCH_2Br}$; the D_{PhCH_2X} values are obtained from ref 15. [e] From ref 14a,b. [f] Assumed to be the same as in acetonitrile. [g] See ref 16. [h] From ref 17. [i] From ref 16b. [j] From the application of eq 5, taking $\Delta S = 1$ meV K^{-1} which corresponds to the formation of two molecules from one and is small and does not vary significantly in the series. [k] The preexponential factor is taken equal to $kT/h = 5 \times 10^{12}$ M^{-1} s^{-1}. [l] In the application of eq 3, $E°_{R^\bullet/R^-}$ was taken as equal to 0.00 V vs SCE[18] and the molar entropies of the charged species (which are the predominant entropic terms) were assumed to compensate each other. [m] From the difference between the exprimental intrinsic barrier and the contribution of bond breaking (intra).

0.1 and 100 V/s. The values of the cleavage rate constants and of the standard potential for the formation of the anion radical were derived from the variation of the peak potentials with scan rate and from the value of the peak width[12] according to a procedure described in the supporting information.

The results (Table 1)[13] are displayed in Figure 1 as a plot of log k (cleavage) vs the standard free energy of the reaction. The latter quantity was estimated as described in Table 1. The standard potentials $E°_{RX/RX^{\bullet-}}$ were obtained from the same experiments (see the supporting information). There is a clear correlation between the rate constants and the standard free energy of the reaction of the type depicted by eq 1 with a value of the average symmetry factor close to 0.5 (0.45). The average intrinsic barrier is 0.70 eV. Why is the intrinsic barrier so large, and why does it depend so weakly upon molecular structure? We may estimate the contribution of the intramolecular bond cleavage by application of eq 3. As seen in Table 1, it represents a modest-to-negligible percentage of the total barrier, particularly for compounds that do not bear ring substituents.

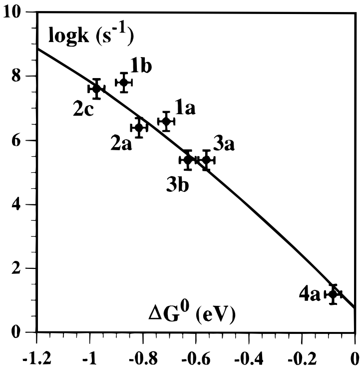

Figure 1. Variation of the cleavage rate constant with the standard free energy of the reaction.

We are thus led to conclude that solvent reorganization is the main factor dictating the height of the intrinsic barrier, contributing 75−100% to the total in the acetophenone series. This observation falls in line with the fact that, in the initial state of the anion radical, the solvent is organized around a negative charge which is mostly concentrated on the carbonyl oxygen and has to reorganize around the negative charge which develops on the leaving group during the reaction. Such values of the solvent reorganization energy are compatible with reasonable values of the two solvation spheres' radii, on the order of 2 Å each, and of the distance between the two centers of charge, on the order of 6 Å. A radius of 2 Å for the solvation sphere of the oxygen carbonyl is also compatible with the small value, 0.14 cm/s, found for the standard rate constant of the electrochemical reduction of acetophenone. Obviously, these estimations are very approximate. Nevertheless, it is noteworthy that the contribution of solvent reorganization to the intrinsic barrier appears to be less with **1a** and **1b**, where charge concentration on the oxygen carbonyl is expected to be less than with the other compounds owing to charge delocalization on the 4-NO_2 and 4-CN groups, respectively.

Supporting Information Available: Cyclic voltammetric data and determination of the cleavage rate constant and standard potential for the formation of the anion radicals from these data (4 pages). See any current masthead page for ordering and Internet access instructions.

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(13) The value found for **3a** is in good agreement with the values recently reported[4c] for an extended series of α-phenoxyacetophenones bearing various substituents on the phenoxy ring, although not a 3-methyl group as in **3a**.

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$$E°_{PhCO_2^-} - E°_{CH_3CO_2^-}\,(V) = D_{PhCO_2-H} - D_{CH_3CO_2-H} + 0.06(pK_{a,PhCO_2H} - pK_{a,CH_3CO_2H})$$

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