Concerted and Stepwise Dissociative Electron Transfers. Oxidability of the Leaving Group and Strength of the Breaking Bond as Mechanism and Reactivity Governing Factors Illustrated by the Electrochemical Reduction of α-Substituted Acetophenones

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Abstract: The cyclic voltammetric investigation of a series of α-substituted acetophenones allowed the identification of the concerted and stepwise character of the dissociative electron transfer reaction, and, in the stepwise cases, the determination of the cleavage rate constants and the standard potentials for the formation of the anion radical. Analysis of the data, using thermodynamical parameters derived from experiment and from literature points to three mechanism governing factors, the oxidability of the leaving group, the bond dissociation energy of the bond being broken, and the LUMO energy. The first of these factors appears to be largely predominant in many cases in the control of the concerted vs stepwise dichotomy. The fluoro substituent provides a reverse example where the bond strength overcomes the unfavorable effect of the leaving group oxidability. It is also an exception, in terms of anion radical cleavage reactivity, where the strength of the C−F bond significantly contributes to slow down the cleavage as opposed to the other substituents where solvent reorganization appears as largely predominant. In the concerted cases, the estimated lifetime of the anion radical is clearly larger than the time of a vibration. The concerted character of the reaction thus results from an energetic advantage rather than from the "nonexistence" of the anion radical intermediate.

The dichotomy between concerted and stepwise mechanisms in dissociative electron transfer

$$\text{concerted:}\quad RX + e^- \rightleftharpoons R^\bullet + X^- \qquad \text{(I)}$$

$$\text{stepwise:} RX + e^- \rightleftharpoons RX^{\bullet -} \text{ (II)} \quad RX^{\bullet -} \rightleftharpoons R^\bullet + X^- \text{ (III)}$$

is an important issue in the understanding and prediction of the type of chemistry that can be triggered upon injecting one electron into a molecule by reaction with homogenous electron donors[2] as well as by electrochemical,[2] photochemical,[3] or pulse radiolytic means.[4]

The competition between the two reaction pathways depends both upon driving force and intrinsic barrier factors. The first of these factors results from the comparison between the standard potentials, $E_1^0 = -D_1 + E^0_{X\bullet/X^-} + T\Delta S$ for the concerted reaction, and $E_2^0 = E^0_{RX/RX\bullet^-}$ for the stepwise reaction (D_1 is the bond dissociation energy in the ground state, ΔS is the corresponding entropy change, and $E^0_{X\bullet/X^-}$ is the standard potential for the oxidation of the leaving group). The difference between these two standard potentials represents the standard free energy for the cleavage of the anion radical:

$$\Delta G_3^0 = -E_1^0 + E_2^0 = D_1 - E^0_{X\bullet/X^-} + E^0_{RX/RX\bullet^-} - T\Delta S \qquad (1)$$

Thus, if the concerted pathway has a stronger driving force than the first step of the stepwise pathway, the cleavage of the anion radical is thermodynamically favorable. It is sometimes considered that stepwise mechanisms are followed when the intermediate (here the anion radical) has a lifetime that is longer than the time for a bond vibration ($\approx 10^{-13}$ s), while concerted mechanisms would occur under the opposite conditions, i.e., when the intermediate "does not exist".[5] However, another point of view has been developed according to which the concerted mechanism is considered to take place when its activation energy is less than that of the stepwise pathway, regardless of the "existence" of the anion radical.[2] Of course, the nonexistence of the anion radical is a sufficient condition for the concerted mechanism to take place but it is not a necessary condition. In

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other words, concerted pathways may be followed under conditions where $RX^{\bullet -}$ has a finite lifetime, i.e., lives longer than a vibration. As shown earlier, the kinetics of the concerted and stepwise reactions may be modeled so as to obey the following activation/ driving force relationships and intrinsic barrier expressions.[2] For each of the three reactions, the activation free energy, $\Delta G^{\ddagger}$, is a quadratic function of the standard free energy of the reaction, ΔG^0

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta G^0}{4\Delta G_0^{\ddagger}}\right)^2 \qquad (2)$$

where $\Delta G_0^{\ddagger}$ is the intrinsic barrier free energy (activation free energy at zero driving force). The reaction standard free energies are $E - E^0_{RX/R^{\bullet}+X^-}$ and $E - E^0_{RX/RX^{\bullet -}}$ for reactions I and II, respectively (E is the electrode potential, the standard potentials being those defined earlier) and $\Delta G^0_{RX^{\bullet -}/R^{\bullet}+X^-}$ for reaction III. For reactions I and III, the intrinsic barrier free energies are related to the bond dissociation energy, D, and to the solvent reorganization factor, λ^0, according to

$$\Delta G_{1\ \text{or3}}^{\ddagger,0} = \frac{D_{1\ \text{or}\ 3} + \lambda^0_{1\ \text{or3}}}{4} \qquad (3)$$

while for reaction II

$$\Delta G_2^{\ddagger,0} = \frac{(D_1^{1/2} - D_3^{1/2})^2 + \lambda_2^0}{4} \qquad (4)$$

In view of the large number of parameters involved, it is not possible to describe the passage from the concerted to the stepwise mechanism by a single equation. We may however find typical examples where the anion radical has a finite lifetime and where, nevertheless, the electrochemical reaction (as investigated for example by mean of cyclic voltammetry) follows a concerted mechanism, at least in the lower part of the range of scan rates.[6] Some such examples where $k_3 = 6 \times 10^{10}$ and 10^{11} s^{-1}, are represented in Figure 1 as peak potentials vs scan rate plots. The procedure for constructing these diagrams are detailed in the Supporting Information based on the analyses in refs 7 and 8. Upon increasing the scan rate, the peak potential shifts toward negative values and the mechanism passes from concerted (noted 1 in Figure 1) to stepwise with, first, reaction III and then reaction II as the rate determining step.

As a general trend, the concerted reaction prevails over the stepwise reaction less easily than predicted on mere thermodynamic grounds. An increase of the driving force of the former at the expense of the latter will nevertheless tend to make the system pass from the stepwise to the concerted mechanism

It follows that weak bonds, poor oxidability of the leaving group, and low energies of the orbital where the incoming electron may be accommodated (usually a π^* orbital) will favor the concerted pathway over the stepwise pathway and *vice versa*. The discriminating role of $E^0_{RX/RX^{\bullet -}}$ has been clearly identified

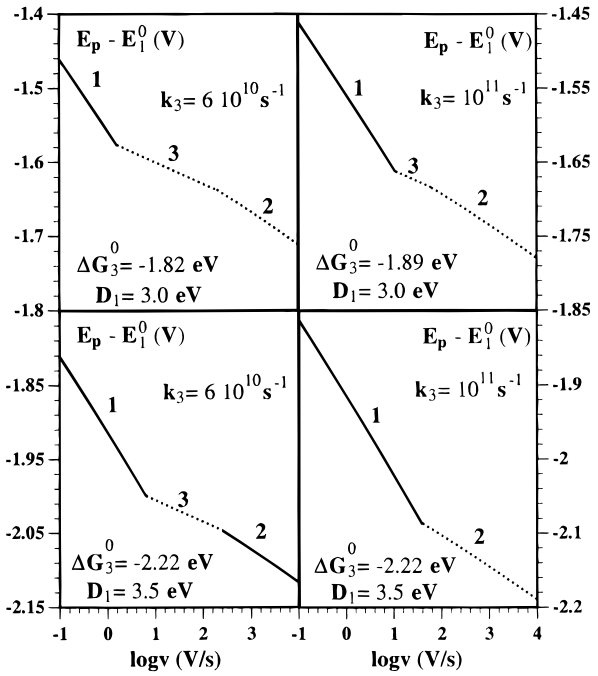
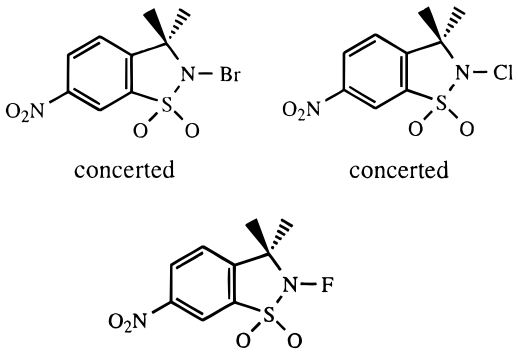


Figure 1. Variation of the cyclic voltammetric peak potential with the scan rate for a concerted (full line) and stepwise (dotted line) reaction. $k_3 = 6 \times 10^{10}$ s^{-1}, $kT/h = 6 \times 10^{12}$ M^{-1} s^{-1}, $\lambda^0_1 = 0.7$, $\lambda^0_2 = 0.5$, $\lambda^0_3 = 0.2$ eV. Diffusion coefficient: 10^{-5} cm^2 s^{-1}, electrochemical frequency factor: 4×10^3 cm s^{-1}. The numbers on each section of the curves denotes the rare determining step.

on experimental grounds in the reduction of arylmethyl halides,[9] aromatic *N*-halosultams[10] and sulfonium cations.[6b] The role of $D_{RX \rightarrow R^{\bullet}+X^{\bullet}}$ was also demonstrated in the latter case. So far, the role of the oxidation potential of the leaving group, $E^0_{X^{\bullet}/X^-}$ has received much less attention. In the case of nitro-substituted *N*-halosultams[10]



the stepwise character of the reaction with F, as opposed to Br and Cl, was attributed to a larger bond dissociation energy. At the same time however, the oxidability of the leaving halide ion changes in a way that would conversely favor the concerted pathway ($E^0_{X^{\bullet}/X^-}$ = 2.62, 1.79, and 1.44 V vs SCE for F, Cl, and Br respectively[11]). It may thus be concluded that, in this series, the effect of bond strength overcompensates the effect of leaving group oxidability.

In order to investigate the combined effect of these two factors in the concerted/stepwise dichotomy and to examine whether

(6) (a) Passage from a concerted to a stepwise mechanism has been observed in the electrochemical reduction of sulfonium cations.[6b] Andrieux, C. P.; Robert, M.; Saeva, F. D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 7864.

(7) (a) Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1973**, *48*, 113. (b) Andrieux, C. P.; Savéant, J.-M. In *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.

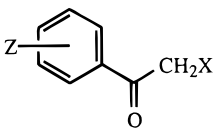
(8) Savéant, J.-M. *J. Phys. Chem.* **1994**, *98*, 3716.

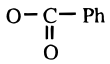
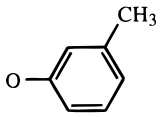
(9) Andrieux, C. P.; Le Gorande, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892.

(10) Andrieux, C. P.; Differding, E.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1993**, *115*, 6592.

(11) See refs 9 and 10.

Chart 1



X	Z		X	Z	
Br	H	**1a**		H	**8a**
	4-NO_2	**1b**			
	4-CN	**1c**		H	**8b**
	4-OCH_3	**1d**			
Cl	H	**2**		H	**8c**
F	H	**3**			
	H	**4a**		H	**8d**
	4-NO_2	**4b**			
	4-OCH_3	**4c**		H	**8e**
	H	**5a**			
	4-CH_3	**5b**		H	**8f**
OCH_3	H	**6a**			
OC_2H_5	H	**6b**		H	**8g**
SPh	H	**7a**			
SC_2H_5	H	**7b**			

the effect of $E^0_{X\bullet/X^-}$ may be predominant, we investigated the electrochemistry in *N*,*N*′-dimethylformamide (DMF) at glassy carbon electrodes of the following series of acetophenones bearing a leaving anionic group in the α-position, and, for some of them, a substituent on the phenyl ring (see Chart 1).

For comparison purposes, earlier results concerning the reduction of α-alkoxy-acetophenones (**6a**,**b**) and α-amino-acetophenones (**8a**−**f**) showing that their anion radicals do not cleave but rather dimerize yielding the corresponding pinacol[12] will also be used in the following discussion.[13]

Results and Discussion

Main Characteristics of the Cyclic Voltammetric Responses. **4b** is the only compound in the whole series that exhibits a single one-electron reversible wave (Figure 2) down to the lowest scan rate (0.1 V/s). From the variation of the peak potential with the scan rate and the value of the standard potential ($E^0_2 = -0.79$ V vs SCE),[14] or from the separation between cathodic and anodic peak potentials (Figure 1),[12c] an apparent standard rate constant of electron transfer (2) of $k^S_2 = 0.22$ cm s^{-1} is found, a value substantially smaller than for usual aromatic compounds.[15] The reason for this relative slowness

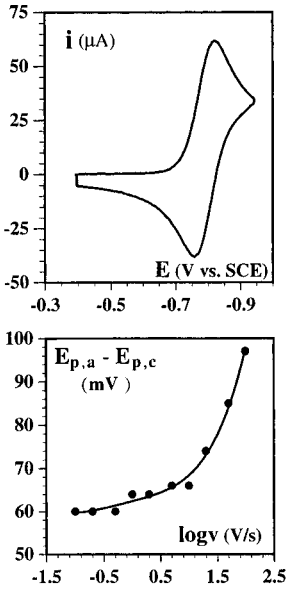


Figure 2. Cyclic voltammetry of **4b** (1.9 mM) in DMF + 0.1 M *n*-Bu_4NBF_4 at a scan rate of 0.1 V/s and variation of the difference between anodic and cathodic peak potentials with the scan rate: temperature, 20 °C; 1 mm-diameter GC electrode.

of electron transfer is the strong localization of the negative charge on the carbonyl oxygen in the anion radical. This interpretation is confirmed by the fact that charge transfer to acetophenone is also relatively slow. A value of 0.14 cm s^{-1} was indeed found from the variations of the cathodic and anodic peak potentials with the scan rate.

All other compounds in the **1**, **2**, **3**, **4**, **5**, and **7** series exhibit two successive waves at low scan rates (below 1 V/s). The first is irreversible, and its height corresponds to the exchange of one electron per molecule. The electron stoichiometry of the first wave was checked by comparison with the one-electron reversible wave of either benzophenone or 4-cyanoacetophenone, which have similar diffusion coefficients. In this determination, the influence of the irreversibility of the first wave of the substituted acetophenone on the peak height was taken into account through the value of the apparent transfer coefficient, α_{ap},[7] ($i_p = 0.496FSC^0D^{1/2}(\alpha_{ap}Fv/RT^{1/2})$ determined from the peak-width (see below). The second is quasi-reversible and corresponds to the reduction of acetophenone (or of the 4-nitro- or 4-cyano-, 4-methoxy- or 4-methyl acetophenones with **1b**, **1c**, **1d**, **4c**, and **5b**, respectively) as verified with authentic samples.[16] The electron stoichiometry of the second wave is half that of the first wave, thus corresponding formally to half-an-electron. The situation is thus quite different from what was found with the **6** and **8** series where there is a single irreversible one-electron wave along which the anion radical dimerizes rather than cleaves.[12] These observations suggest the reduction mechanism depicted in Scheme 1 where the one-electron and half-an-electron stoichiometries at the first and second waves derive from the reaction of the acetophenone enolate formed at the first wave along a two-electron process with one molecule of starting material.

In line with this reaction mechanism, the first irreversible peak doubles in height when a strong enough acid is added to the solution. Figure 3 gives an example of this behavior in the case of **4a** with addition of phenol. The second wave represents the reduction of the acetophenone generated at the first wave. In the absence of acid, its height corresponds to 0.5 electron in agreement with the above reaction scheme. Upon addition of the acid it grows up to two electrons which falls also in line with Scheme 1, taking into account the fact that acetophenone

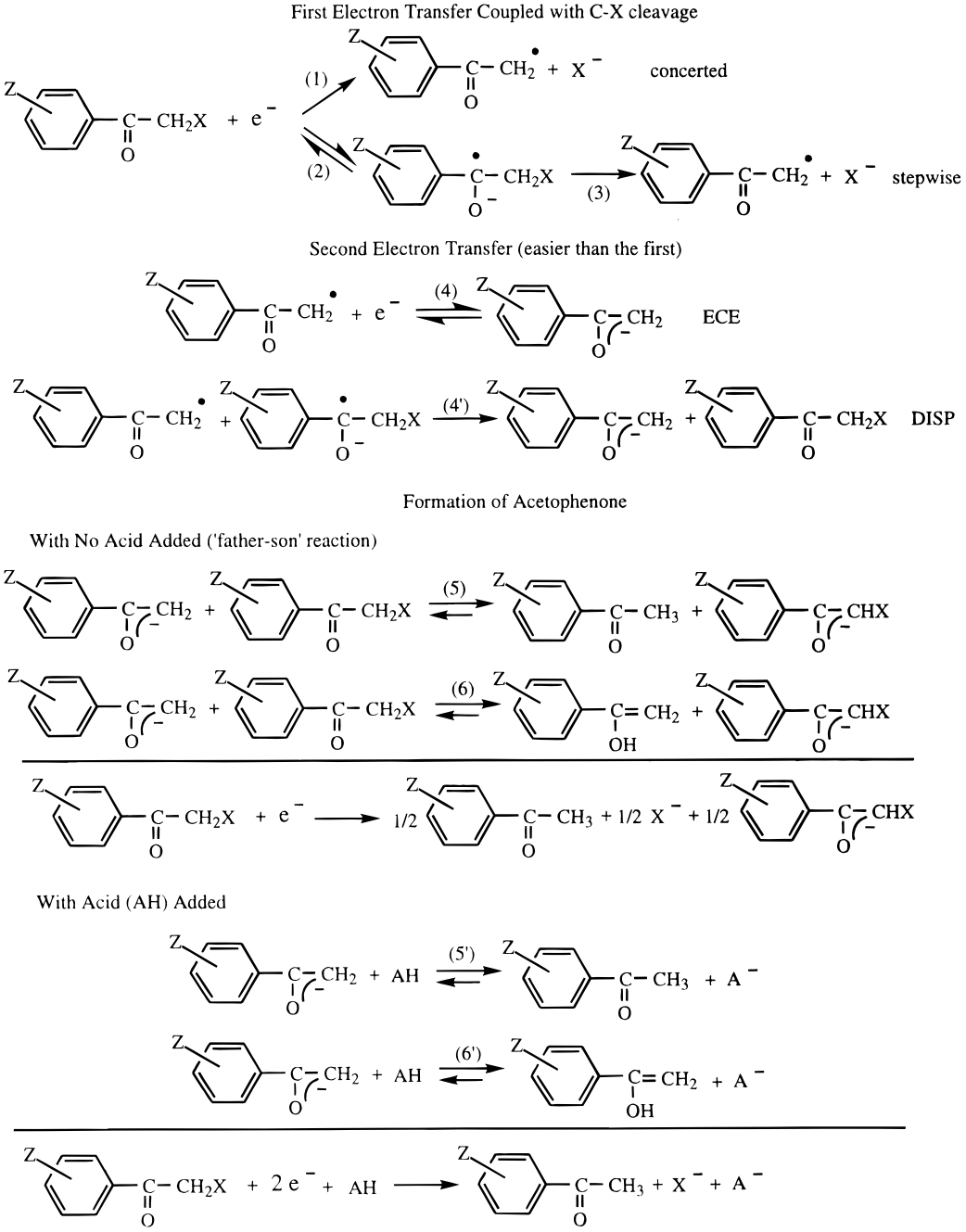
(12) Andrieux, C. P.; Savéant, J.-M. *Bull. Soc. Chim. Fr.* **1972**, 3281.

(13) (a) Cleavage of several substituted acetophenone ketyls generated by homogeneous electron donors has also been investigated (see ref 13b and references cited therein) as well as for electrogenerated arylcyclopropyl acetophenone ketyls (see reference 13c and references cited therein). More recently, the cleavage rate constants of anion radicals of acetophenones bearing various phenoxy α-substituents have been reported.[13d] (b) Tanner, D. D.; Chen, J. J.; Chen, L.; Luelo, C. *J. Am. Chem. Soc.* **1991**, *113*, 8074. (c) Tanko; J. M.; Drumright, R. E.; Sulemen, N.; Brammer, L. E. *J. Am. Chem. Soc.* **1994**, *116*, 1585. (d) Andersen, M. L.; Mathivanan, N.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1996**, *118*, 4871.

(14) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

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

Scheme 1



undergoes a $2e^- + 2H^+$ reduction in acidic medium.[16b] Table 1 summarizes several examples where the same behavior was found.

The reason that we have included in Scheme 1 the formation of the enol of acetophenone (reactions 6 and 6′) concurrently with the formation of acetophenone itself (reactions 5 and 5′) from the common enolate/carbanion intermediate derives from high scan rate cyclic voltammetric experiments where the kinetics of these reactions manifest themselves upon raising the scan rate. At lower scan rates the thermodynamically favorable formation of acetophenone predominates and therefore the enol does not appear in the stoichiometric balances of Scheme 1. This point is not central to our discussion of the concerted vs stepwise dichotomy. Its detailed analysis will be published elsewhere.

Assignment of the Cleavage Mechanism. In the investigation of the concerted vs stepwise dichotomy, the simplest characterization is that of the stepwise mechanism. Evidence for the intermediacy of the anion radical can be obtained in two ways. When its lifetime is not too short, direct evidence can be gained if the first wave becomes reversible upon raising the scan rate, while, simultaneously, the acetophenone wave should disappear. This is what is observed with **7b** at 20 °C, where reversibility is reached at a rather low scan rate, 10 V/s (Figure 4). The fact that the acetophenone wave appears at a low scan rate beyond the reduction wave of **7b** is a clear indication that its anion radical does cleave rather than dimerizes as occurs for compounds **6** and **8**.[12] At 20 °C, none of the other compounds exhibits any reversibility up to scan rates as high as 30 000 V/s using a gold ultramicroelectrode.[17] However, with **5a**, upon lowering the temperature down to −16 °C,

(16) (a) The acetophenone wave is not entirely reversible because of dimerization of the anion radicals leading to the pinacolate.[16b] (b) Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1971**, *3*, 419.

(17) Andrieux, C. P.; Hapiot, P.; Savéant, J.-M. *Chem. Rev.* **1990**, 90, 723.

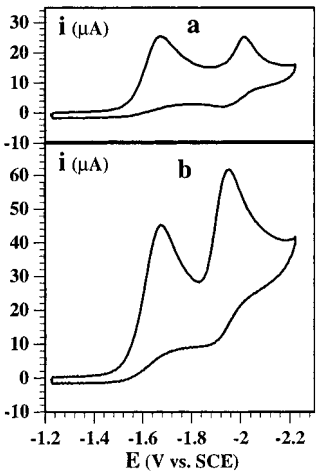


Figure 3. Cyclic voltammetry of **4a** (1 mM) in DMF + 0.1 M *n*-Bu_4NBF_4 at a scan rate of 0.2 V/s in the absence of acid (a) and in the presence of 5 mM phenol: temperature, 20 °C; 3mm-diameter GC electrode.

Table 1. Addition of Acids

compd (concn in mM)	acid (concn in mM)
1a (2)	CF_2HCO_2H (2)
1d (2)	CF_2HCO_2H (2)
2 (2)	CF_2HCO_2H (2)
3 (1.1)	CH_3CO_2H (4)
4a (1)	PhOH (5)
7a (2)	PhOH (10)
7b (1.3)	PhOH (3)

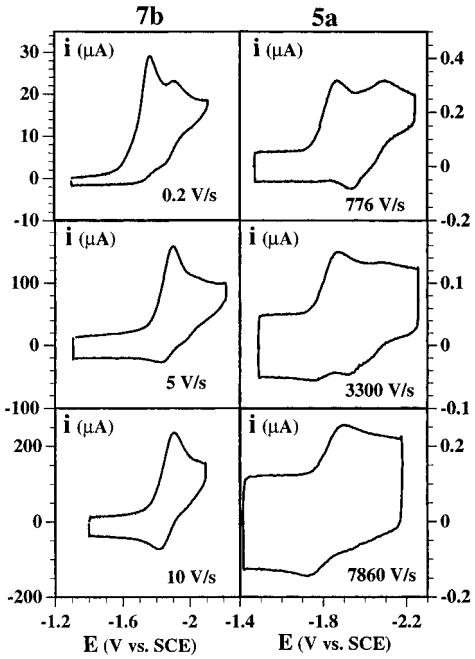


Figure 4. Cyclic voltammetry (in DMF) of **7b** (1.3 mM), 0.1 M *n*-Bu_4NBF_4, at a GC disk electrode, temperature, 20 °C, and of **5a** (2.9 mM), 0.4 M Et_4NBF_4, at a gold disk electrode, diameter, 25 μm (a), 10 μm (b, c), temperature, −16 °C.

reversibility is reached at 8000 V/s (Figure 4). Similar observations were made with **5b**, where full reversibility at −20 °C is reached at 22 855 V/s (see Supporting Information). In these three cases, the reduction thus follows a stepwise mechanism.

In cases where the reduction wave is irreversible over the whole range of accessible scan rates, another approach to the mechanism consists in the observation of the variation of the peak potential, E_p, with the scan rate and of the values of the half peak width, $E_{p/2} - E_p$. In order to keep ohmic drop negligible, two GC disk electrodes were used successively: a 3 mm-diameter electrode between 0.1 and 10 V/s (open squares in Figures 5 and 6) and a 1 mm-diameter electrode between 10 and 100 V/s (open circles in Figures 5 and 6). In order to free the data from the kinetic influence of the follow-up protonation steps they should be gathered either with no acid added, in which case the electron stoichiometry is 1, or with addition of acid in sufficient concentration for the electron stoichiometry to reach 2. Some typical results are shown in Figure 5.

If, in the stepwise mechanism (reactions II and III), the rate determining step is reaction III while reaction II remains at equilibrium the peak potential varies linearly with logv with a slope $\partial E_p/\partial \log v = 29$ mV at 20 °C, while the peak width $E_{p/2} - E_p = 47$ mV at the same temperature.[7] Conversely, if reaction II is the rate determining step, $\partial E_p/\partial \log v = (29/\alpha_2)$ while $E_{p/2} - E_p = (47/\alpha_2)$ mV. Increasing the scan rate makes the kinetics pass from the former situation to the latter.[7] We may thus derive from the peak width data an apparent transfer coefficient $\alpha_{ap} = 47/(E_{p/2} - E_p)$ that is expected to vary from 1 to α_2 (which should be close to 0.5) when the kinetic control passes from reaction III to reaction II. We have already noted that electron transfer to acetophenone is not very rapid. It follows that mixed kinetic control by reactions II and III is likely to be encountered in the present series of compounds. It is thus possible to use as diagnostic criterion of the stepwise mechanism, the observation that α_{ap} is larger than 0.5 in a significant portion of the range of scan rates explored. For more precision in the mechanism diagnosis, it is desirable to jointly use the E_p −log v data and $E_{p/2} - E_p$ data. This was done by testing the consistency of the E_p −log v and $E_{p/2} - E_p$ data according to a procedure described in details in the Supporting Information. That this test of consistency leads to satisfactory results can be seen in Figure 5 by the fact that the solid line in the upper diagrams representing the theoretical reconstruction of the E_p −log v variation from the $E_{p/2} - E_p$ data passes through the E_p −log v points within experimental uncertainty. For **5a**, the occurrence of the stepwise mechanism at −16 °C was demonstrated by the reversibility observed upon raising the scan rate (Figure 4). The same conclusion holds at 20 °C as results from the E_p −log v and $E_{p/2} - E_p$ data. This is also true for **1c** and **3**, where reversibility could not be reached even at low temperature. Figures similar to Figure 5 for all the other compounds of the same category can be found in the Supporting Information. The mechanistic conclusions are summarized in Table 2. The above test of consistency of the E_p −log v and $E_{p/2} - E_p$ data also provides the value of the two parameters

$$C_1 = \log(Fk_3D^2/2RTk_{S,2}^4) \quad (5)$$

and

$$C_2 = E_2^0 + (RT \ln 10/F) \log(2k_3D/k_{S,2}^2) \quad (6)$$

(see Supporting Information), from the values of which k_3 and E^0 may be derived provided the value of $k_{S,2}$ can be estimated. $k_{S,2}$ was taken as equal to 0.14 cm/s, the value for acetophenone, for **3**, **4a, 4c**, **5a,** and **5b** and to 0.22 cm s^{-1}, the value for the nitro-derivative **4b**, for **1b** and **1c**. Because the cyclic voltammogram of **7b** ceases to be irreversible upon raising the scan rate, the foregoing treatment is not applicable to this particular compound. In this case, the values of k_3 and E_2^0 were derived by direct simulation of the voltammograms. The simulation also provides the value of $k_{S,2}$, 0.16 cm s^{-1}, which lies, as expected, in between the values found for acetophenone, and

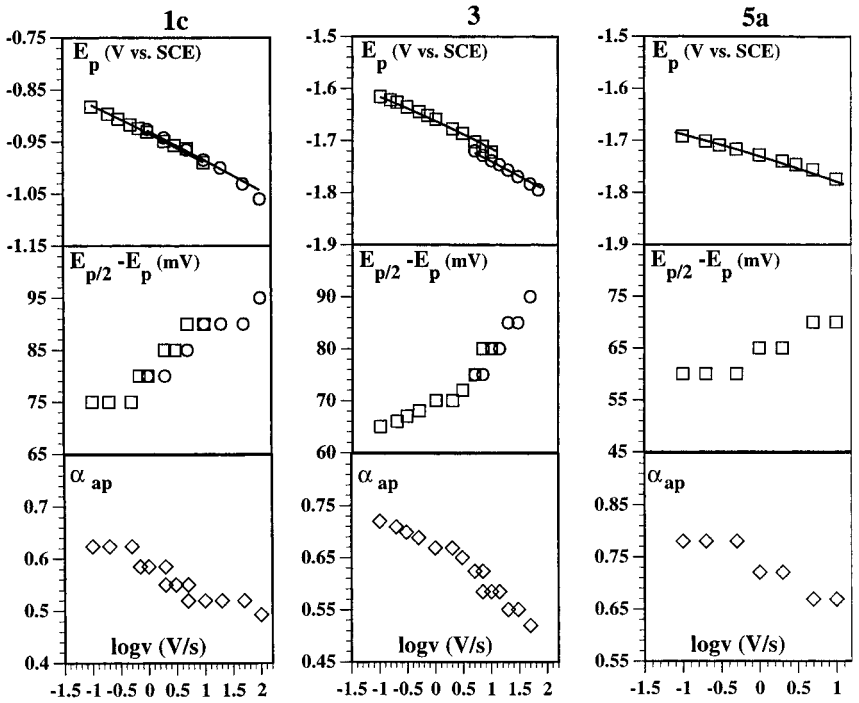


Figure 5. Cyclic voltammetric peak characteristics of **1c** (1 mM), **3** (1 mM) and **5a** (1 mM,) in DMF + 0.1 M *n*-Bu_4NBF_4, at a 3 mm (□) and 1 mm (○) diameter glassy carbon electrode: temperature, 20 °C. The lower diagrams represent the values of α_{ap} derived from the peak width. The solid lines in the top diagrams represent the variations of E_p derived from the peak width values according to the procedure described in the text and in the Supporting Information.

Table 2. Reductive Cleavage Mechanism

compd	mechanism
1a	concerted
1b	stepwise
1c	stepwise
1d	concerted
2	concerted
3	stepwise
4a	stepwise
4b	stepwise
4c	stepwise
5a	stepwise
5b	stepwise
7a	stepwise
7b	stepwise

Table 3. Standard Potentials and Cleavages Rates for the Stepwise Reactions

compd	C_1 (log(s/V))	C_2 (V vs SCE)	log k_3 (s^{-1})	$-E^0$ (V vs SCE)
1b	0.50	−1.35	6.6	0.83
1c	1.83	−0.79	7.8	1.04
3	0.79	−1.57	6.1	1.75
4a	1.15	−1.61	6.4	1.81
4c	2.33	−1.70	7.6	1.97
5a	0.10	−1.67	5.4	1.81
5b	0.10	−1.74	5.4	1.88
7a	1.00	−1.58	6.1	1.77
7b			1.2[a]	1.87[a]

[a] From the CV reversibility data in Figure 4.

4b. The results obtained for the whole set of compounds undergoing a stepwise reaction are listed in Table 3.

Compounds **1a**, **1d**, and **2** exhibit a different behavior (Figure 6) indicating that the reduction is controlled by an electron transfer reaction, either I or II, with a value of α_{ap} clearly below 0.5. In these cases, the test of consistency of the E_p and $E_{p/2} - E_p$ data (see Supporting Information) simply consists in the application of the two equations relating each of these to the transfer coefficient, α, which is now a true transfer coefficient:

$$\alpha = \frac{1.857\ RT}{F(E_{p/2} - E_p)}$$

$$E_p = E^0 - 0.78\frac{RT}{\alpha F} + \frac{RT}{\alpha F}\ln\left(\frac{k_s}{\sqrt{\alpha F \upsilon D/RT}}\right)$$

Inspection of Figure 6 shows that the consistency between the two sets of data is again satisfactory. The fact that α is significantly smaller than 0.5 in all three cases is a first indication that the reduction of these compounds follows a concerted mechanism. Indeed, according to the theory of dissociative electron transfers recalled in the introduction, the intrinsic barriers are usually large because they are mostly governed by the dissociation energy of the bond being broken. It follows that the reduction takes place at a potential much more negative than the dissociative electron transfer standard potential, $E^0_{RX/R^{\bullet}+X^-}$, and therefore that the transfer coefficient (symmetry factor)

$$\alpha = 0.5\left(1 + \frac{E - E^0_{RX/R^{\bullet}+X^-}}{4\Delta G_0^{\ddagger}}\right) \qquad (7)$$

should be significantly smaller than 0.5. This conclusion may be confirmed as follows. Because of inductive effects, the standard potential for the formation of the anion radical of **1a**, **1d**, and **2** is expected to be more negative than that of **3**. Thus if the reduction of **1a**, **1d**, and **2** were to follow a stepwise mechanism, kinetically controlled by reaction II, their peak potentials given by

$$E_{p,2} = E^0_2 - 0.78\frac{RT}{\alpha F} + \frac{RT}{\alpha F}\ln\left(\frac{k_{s,2}}{\sqrt{\alpha F \upsilon D/RT}}\right)$$

should be more negative than

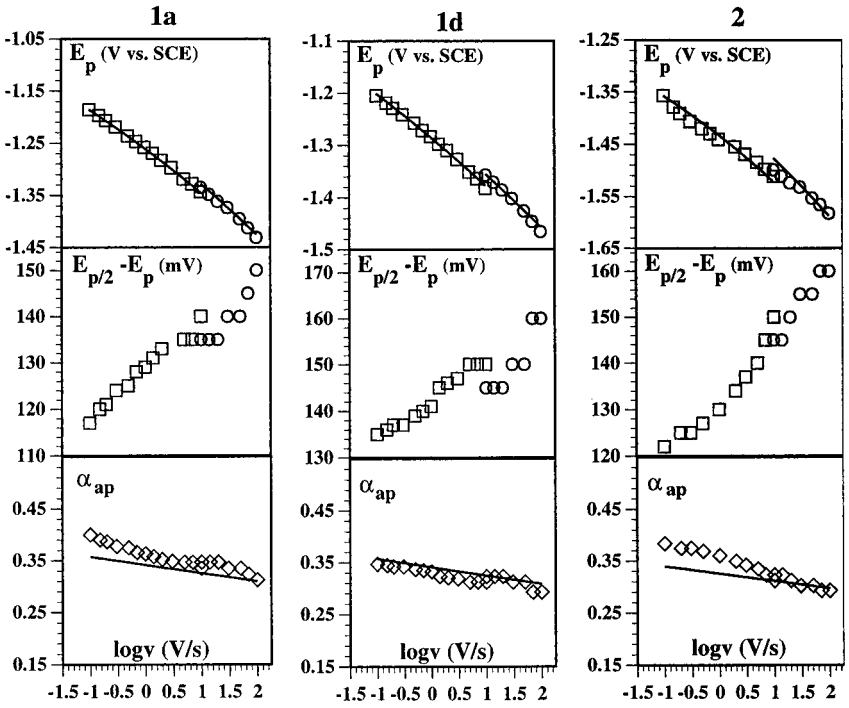


Figure 6. Cyclic voltammetric peak characteristics of **1a** (2 mM,), **1d** (2 mM), and **2** (2 mM) in DMF + 0.1 M *n*-Bu_4NBF_4 + 2 mM CF_2HCO_2H, at a 3 mm (□) and 1 mm (○) diameter glassy carbon electrode: temperature, 20 °C. The lower diagrams represent the values of α derived from the peak width. The solid lines in the top diagrams represent the variations of E_p derived from the peak width values according to the procedure described in the text. The solid lines in the lower diagrams represent the predicted values of α_{ap} according to eq 7.

$$E_2^0(3) - 0.78\frac{RT}{\alpha F} + \frac{RT}{\alpha F}\ln\left(\frac{k_{s,2}}{\sqrt{\alpha F v D/RT}}\right)$$

The solid line in Figure 7 represents this maximized variation using the data in Table 3, taking D = 10^{-5} cm^2 s^{-1}, α = 0.5, and $k_{S,2}$ = 0.14 cm s^{-1} (the value for acetophenone). The actual E_p values are thus in average at least 430, 400, and 250 mV more positive than predicted for a stepwise mechanism. Equivalently, the stepwise mechanism would imply that the heterogeneous standard rate constant of reaction II would be larger than 1028, 382, and 20 cm/s for **1a**, **1d**, and **2**, respectively. Obviously, these values are absurdly large; the heterogeneous standard rate constant for the reduction of anthracene in DMF, one of the fastest electron transfer reaction, is only 3 cm/s.[18] We can thus safely conclude that the reduction of these three compounds follows a concerted mechanism as reported in Table 2.

Relationships between Molecular Structure, Mechanism, and Reactivity. In order to establish these relationships we need to extract a series of parameters from the experimental data and gather others from the literature.

For the compounds following a concerted mechanism, the bond dissociation energy (BDE) of the starting molecule, RX, may be derived from the value of the peak potential and the value of the standard potential for the oxidation of the leaving group, $E^0_{X^{\bullet}/X^-}$ (Table 4). For example, at 0.1 V/s[9,10]

$$D_1 = \frac{2}{3}(E^0_{X^{\bullet}/X^-} - E_p) + 0.3 \qquad (8)$$

The BDE of **1a** and **2** thus obtained are significantly smaller than those of the corresponding benzyl halides, 2.52 and 3.12 eV, respectively[9,21] pointing to a greater stability of the phenacyl radical as compared to the benzyl radical as expected from the following resonant forms

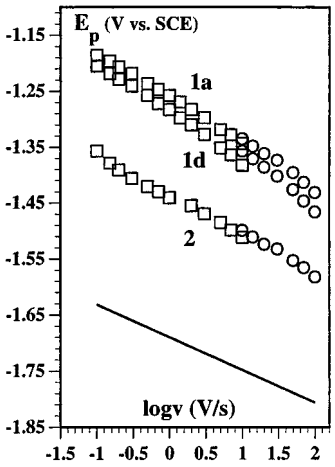


Figure 7. Predicted maximized variation of the peak potential variation with scan rate for **1a**, **1d**, and **2** if they were to follow a stepwise mechanism (solid line) as compared to the experimental variations (open squares and circles).

(18) Andrieux, C. P.; Garreau, D.; Hapiot, P.; Savéant, J.-M. *J. Electroanal. Chem.* **1988**, *248*, 448.

(19) (a) A reliable value, 1.06 V vs SCE, is available for $CH_3CO_2^-$,[19b] but not for $PhCO_2^-$. The value given in ref 19b, 0.36 V vs SCE, is smaller than for $CH_3CO_2^-$, which seems counterintuitive in view of the fact that $CH_3CO_2^-$ is a stronger base than $PhCO_2^-$ (the pK_a's in acetonitrile are 22.3 and 20.7, respectively[19c,d]). Starting from the E^0 value of $CH_3CO_2^-$, we estimated the value for $PhCO_2^-$ from the following equation

$$E^0_{PhCO2-} - E^0_{CH3CO2-}\ (V)\ D_{PhCO_2^-H} - D_{CH_3CO_2^-H} + 0.06\ (pK_{a,PhCO_2H} - pK_{a,CH_3CO_2H})$$

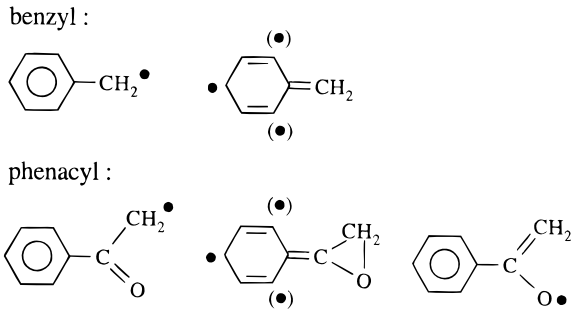
assuming that the entropic terms, $\Delta S_{RX/R^{\bullet}+H^{\bullet}}$, are *ca.* the same in both cases. (b) Eberson, L. *Acta Chem. Scand B* **1984**, 439. (c) Kolthoff, I. M.; Chantoni, M. K.; Bhownik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23. (d) Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 76.

(20) (a) Hapiot, P.; Pinson, J.; Yousfi, N. *New J. Chem.* **1992**, *16*, 877. (b) Andrieux, C. P.; Hapiot, P.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1993**, *115*, 7783.

Table 4. Reactivity Data[a]

compd	D_1	$E^0_{X\bullet/X^-}$	$-E^0_{Rx/Rx\bullet-}$	log k_3 (s^{-1})	$-\Delta G^0_3$	$-E_p$[b] concerted	$-E_p$[b] stepwise
concerted	*c*	*e*	predicted	predicted		exp[al]	predicted
1a	2.05	1.44	1.76−2.01	10.1−11.0	1.32−1.57	1.19	1.46−1.71
2	2.40	1.79	1.76−2.01	10.1−11.0	1.32−1.57	1.36	1.46−1.71
1d	2.07	1.44	1.76−2.15	10.0−11.4	1.30−1.69	1.20	1.46−1.85
stepwise	*d*		exp[al]	exp[al]		predicted	exp[al]
1b	1.85	1.44[e]	0.83	6.6	0.59	0.89	0.64
1c	1.90	1.44[e]	1.04	7.8	0.75	0.96	0.88
3	3.12−3.46	2.62[e]	1.75	6.1	1.20−1.54		1.61
4a	2.53	1.24[f,g]	1.81	6.4	0.70	2.10	1.67
4b	2.53	1.24[f,g]	0.79	(−0.9)[m]	−0.15	2.10	0.82
4c	2.53	1.24[f,g]	1.97	7.6	0.86	2.10	1.82
5a	1.78	0.24[f,h]	1.81	5.4	0.44	1.98	1.69
5b	1.78	≈0.24	1.88	5.4	0.51	2.06	1.76
6a	2.56	0.06[f,i]	1.80[l]	(−2.8)[m]	−0.53	3.33	1.8
6b	2.57	≈0.06	1.80[l]	(−2.9)[m]	−0.54	3.35	1.8
7a	1.77	0.10[f,j]	1.77	6.1	0.27	2.11	1.64
7b	2.14	0.06[f,i]	1.87	1.2	−0.04	2.70	1.84
8d	2.67	≈−1.0[k]	1.83[l]	(−18.8)[m]	−1.87	4.76	1.83

[a] Energies in eV, potentials in V vs SCE. [b] At 0.1 V/s. [c] Estimated as described in the text. [d] From the experimental E_p data. [e] See footnote 11. [f] Assumed to be the same as in acetonitrile. [g] See footnote 11. [h] From ref 20a. [i] From ref 19b. [j] From ref 20b. [k] For i-Pr_2N^- in THF, from ref 19b. [l] From ref 12. [m] Estimated (see text).



It also appears that the difference in BDE is larger for the chloro (0.72 eV) than for the bromo (0.47 eV) derivative. This observation may be interpreted in terms of repulsive dipole−dipole interactions in the starting molecule ($^{\delta+}$C=O$^{\delta-}$ against $^{\delta'+}$C-X$^{\delta'-}$) which are expected to be larger with Cl than with Br. Assuming that these interactions are weak for Br, we may estimate the BDE s of the other α-substituted acetophenones, **4a**, **5a**, **6a**, **6b**, **7a**, and **7b**, from the following equation

$$D_{PhCOCH_2X} = D_{PhCH_2X} - D_{PhCH_2Br} + D_{PhCOCH_2Br}$$

using for the α-substituted toluenes the values gathered from ref 21. For **1b** and **1c**, the value for **1a** has been corrected for the weakening of the bond by electron-withdrawing para substituents as for the corresponding benzyl bromides.[9,22] As seen with **1d** and with the corresponding substituted benzyl bromides, the effect of electron-donating para substituents, such as CH_3 and CH_3O, is weak. The same value of D_1 as for **4a** and **5a** was therefore taken for **4c** and **5b**, respectively. The BDE of **3** cannot be derived from that of **1a** according to the above procedure since the dipole−dipole interactions in **3** are expected to be strong, even stronger than in **2**. The only piece of knowledge we have for the moment is that $D_{PhCOCH_2F} < D_{PhCH_2F} - D_{PhCH_2Cl} + D_{PhCOCH_2Cl}$, i.e., the BDE of **3** is smaller than 3.46 eV. For the compounds that follow a stepwise mechanism, the free energy of reaction III, ΔG^0_3, can be derived (Table 4) from the values of D_1, $E^0_{X\bullet/X^-}$, $E^0_2 = E^0_{RX/Rx\bullet-}$ and ΔS according to eq 1. The latter term corresponds to the formation of two particles out of one. It is about constant in the series and equal in average to 0.59 meV K^{-1}. As seen in Figure 8, there is a good correlation, obeying eq 2, between the cleavage rate constant and the driving force of the reaction with the exception of **3** and **7a** which we will discuss later on. The very existence of the correlation and the fact that it is endowed with a large intrinsic barrier has been discussed elsewhere[23] in terms of solvent reorganization attending the displacement of the negative charge from the carbonyl oxygen to the leaving group as the cleavage proceeds.

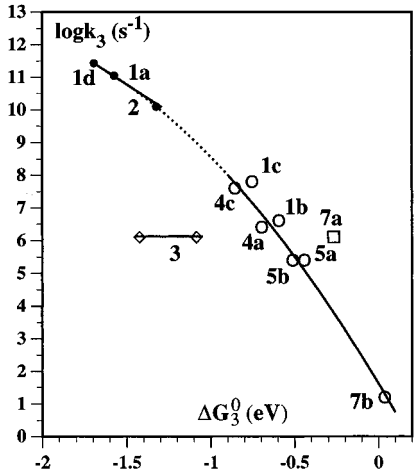


Figure 8. Compounds reduced according to a stepwise mechanism (○, □, and ◇). Experimental variation of the cleavage rate constant with the standard free energy of the reaction. Estimation of the anion radical cleavage rate constants for the compounds reduced according to a concerted mechanism.

We may use this correlation to estimate what would have been the values of k_3 for compounds **1a**, **1d**, and **2** (Table 4) if their reduction had followed a stepwise rather than a concerted mechanism. This estimation requires the value of ΔG^0_3 for each of these three compounds and thus of $E^0_2 = E^0_{RX/RX\bullet-}$. For **1a** and **2,** the latter parameter can be bracketed between the values for **3** and for acetophenone, and, for **1d**, between the values for **3** and for 4-methoxyacetophenone (−2.15 V vs SCE). The values of ΔG^0_3 listed in Table 4 ensue. k_3 is then

(21) (a) Benson, S. N. *Thermochemical Kinetics*; Wiley: New York, 1976. (b) *Handbook of Chemistry and Physics*, 72nd ed.; CRC: Cleveland, OH, 1991−1992, pp 9−121.

(22) Clark, K. B.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1991**, *113*, 9363.

(23) Andrieux, C. P.; Savéant, J.-M.; Tallec, A.; Tardivel, R.; Tardy, C. *J. Am. Chem. Soc.* **1996**, *118*, 9788.

bracketed by means of the extrapolation procedure depicted in Figure 8. In all three cases the predicted values of k_3, albeit large, are clearly below 10^{13} s^{-1}, pointing to the conclusion that the reduction of these three compounds follows a concerted mechanism in spite of the fact that their anion radicals "exist" thus illustrating the discussion of this point given in the Introduction.

We may also, from these predicted values of k_3, bracket the peak potential (at 0.1 V/s) that would have been observed if the reduction of compounds **1a**, **1d**, and **2** had followed a stepwise mechanism, assuming, as seems reasonable, that $k_{S,2}$ is close to that of acetophenone. To achieve this estimation, we used a procedure that is the reverse of the procedure that was used earlier to estimate k_3 and E^0_2 from the peak potential data for the real stepwise reactions. Namely, the value of log $\upsilon + C_1$ is derived from the values of k_3 and $k_{S,2}$ according to eq 5. Then, the value of the $E_p - C_2$ is obtained from the theoretical relationship between this parameter and log $\upsilon + C_1$ (Figure S3a in the Supporting Information section). Deriving C_2 from the values of k_3, $k_{S,2}$, and E^0_2 finally provides the value of E_p. As expected with such fast follow-up reactions, the peak potential is entirely governed by the forward electron transfer step, i.e., by the values of $k_{S,2}$ and E^0_2. For all three compounds (Table 4), the peak potential values thus predicted are much more negative than the experimental values thus confirming that their reduction does follow a stepwise mechanism. We also see, in the lower diagrams of Figure 7, that the values of α derived from eq 7 in the framework of a concerted mechanism (using eq 8 and the numbers in Table 4) are in satisfactory agreement with the experimental values.

Conversely, for the compounds that follow a stepwise mechanism, the value of the peak potential (at 0.1 V/s) that would have been observed if their reduction had followed a concerted mechanism may be estimated, with the exception of **3**, by application of eq 8 (Table 4). In all cases, the "concerted peak potentials" are much more negative than the experimental peak potentials thus providing a further confirmation of the reduction mechanism. For the compounds that give rise to an anion radical which is stable in the whole range of scan rates, such as **4b**$^{\bullet-}$, or that dimerizes rather than cleaves, such as **6a**$^{\bullet-}$, **6b**$^{\bullet-}$, **8d**$^{\bullet-}$, the driving force for cleavage may be estimated by application of eq 1, and, from it, the predicted values of k_3, using the log$k_3 - \Delta G^0_3$ correlation established earlier (Figure 8). These are very approximate estimations since the values of $E^0_{X\bullet/X^-}$ are themselves very approximate (Table 4). Nevertheless, the very low values of k_3 thus predicted allows one to understand why these compounds do not undergo any significant cleavage. The fact that **4b**$^{\bullet-}$ does not dimerize, whereas **6a**$^{\bullet-}$, **6b**$^{\bullet-}$, and **8d**$^{\bullet-}$ do, may be explained by the presence of the nitro group in para which leaves little unpaired electron density on the carbonyl carbon.

The case of **3** is worth some additional comments. An upper limit of the BDE has already been obtained. A lower limit may be derived from the very fact that its reduction follows a stepwise rather than a concerted mechanism. The value of D_1 that would give rise, for a concerted mechanism, to the same peak potential value as observed experimentally is 3.12 eV. The BDE of **3** should thus lie between 3.12 and 3.46 eV.

We may now examine what are the molecular factors that govern the occurrence of the concerted vs the stepwise mechanism. Among the compounds deriving from acetophenone with no ring substituents, there is no large variation of the standard potential $E^0_{RX/RX\bullet-}$. The main factors that govern the concerted/stepwise dichotomy are therefore D_1 and $E^0_{X\bullet/X^-}$. According to eq 8, an increase of D_1 makes the predicted peak potential becomes more negative, with a 1.5 coefficient, thus favoring the stepwise mechanism over the concerted mechanism. A decrease of $E^0_{X\bullet/X^-}$ has the same effect with a unity coefficient. Table 5 summarizes the contributions of these two factors which make the various compounds of the acetophenone series follow a stepwise mechanism by comparison with the two compounds in the same series, **2** and **1a**, which undergo a concerted mechanism. Inspection of Table 5 reveals that, with the exception of **3**, the stepwise mechanism (or a noncleaving mechanism) is followed predominantly because of the poor oxidability of the leaving group rather than because of a strengthening of the cleaving bond. There are even cases, such as **5a**, **7a** (compared with both **2** and **1a**), and **7b** (compared with **2**), where the BDE factors plays against the stepwise mechanism but is overcompensated by a decrease in the leaving group oxidability.

Table 5. Factors Governing the Concerted/Stepwise Dichotomy in the Acetophenone Series[a]

	comparison with **2**		comparison with **1a**	
compd	$-1.5\Delta D_1$[b]	$\Delta E^0_{X\bullet/X^-}$[c]	$-1.5\Delta D_1$[d]	$\Delta E^0_{X\bullet/X^-}$[e]
3	−1.08/−1.59	0.83	−1.61/−2.11	1.18
4a	−0.20	−0.55	−0.72	−0.20
5a	0.93	−1.55	0.40	−1.20
6a	−0.24	−1.73	−0.77	−1.38
6b	−0.26	−1.73	−0.78	−1.38
7a	0.94	−1.69	0.41	−1.34
7b	0.39	−1.73	−0.14	−1.38
8d	−0.41	−2.99	−0.93	−2.64

[a] Energies in eV, potentials in V vs SCE. [b] $\Delta D = D_{PhCOCH_2X} - D_{PhCOCH_2Cl}$. [c] $\Delta E^0_X = E^0_{X\bullet/X^-} - E^0_{Cl\bullet/Cl^-}$. [d] $\Delta D = D_{PhCOCH_2X} - D_{PhCOCH_2Br}$. [e] $\Delta E^0_X = E^0_{X\bullet/X^-} - E^0_{Br\bullet/Br^-}$.

3 is a counter example to these rules; in spite of the large uncertainty on its determination, it is seen that the BDE is the dominant factor is the increase of this factor, while the leaving group oxidability factor plays against the stepwise mechanism, as was already observed with *N*-halonitrosultams (see Introduction).

The fact that **1b** and **1c** follow a stepwise mechanism, whereas **1a** and **1d** undergo a concerted mechanism, is a reflection of the decrease of the standard potential for the formation of the anion radical (which is a measure of the LUMO energy) which overcomes a small decrease of the BDE. The situation is very similar to what has been observed previously with benzyl halides[9] and *N*-halosultams.[10]

As seen in Figure 8, the points representing **3** and **7a** fall clearly out of the correlation between the kinetics and thermodynamics of the anion radical cleavage. The fact that the data point for **3** falls (even with a large uncertainty in the value of the driving force) much below the correlation line may be explained within the interpretation already given for the other anion radicals.[23] It was shown that the intrinsic barrier

$$\Delta G^{\ddagger}_0 = \frac{D_{RX\bullet-} + \lambda^0}{4}$$

consists in a intramolecular cleavage contribution, $D_{RX\bullet-}/4$, and a solvent reorganization contribution, $\lambda^0/4$. From the data in Figure 8, the total intrinsic barrier may be bracketed between 0.89 and 1.02 eV. The intramolecular cleavage contribution[8,23]

$$D_{RX\bullet-}/4 \approx (D_{RX} + E^0_{RX/RX\bullet-} - E^0_{R\bullet/R-})/4$$

lies between 0.34 and 0.43 eV, and thus the solvent reorganization contribution is in between 0.55 and 0.59 eV, i.e., 61−58% of the total. Both contributions are larger than for the other

anion radicals of the acetophenone series.[23] Concerning the intramolecular cleavage contribution, this is essentially a consequence of the fact than the C−F bond in the parent molecule is the strongest of the whole series. The increased solvent reorganization energy is the result of the small size of the fluoride ion on which the charge, initially located on the carbonyl oxygen, is transferred upon cleavage.

In the case of **7a**$^{\bullet-}$, the intramolecular reorganization is negligible and the solvent reorganization contribution is 0.57 eV, significantly smaller than with the other compounds (0.7 eV). This observation may be explained by the fact that the charge is less localized than with the other acetophenones when it is transferred from the carbonyl oxygen to the leaving group where delocalization between the sulfur atom and the phenyl ring may take place. It is presumably for the same reason that the data point for **5a** is somewhat above the correlation line due to some delocalization over the phenoxy moiety, albeit to a lesser extend than in the PhS case. With **5b**, such an effect is expected to be counteracted by some more charge localization on the carbonyl oxygen in the initial state under the influence of the electron donating 4-methyl group.

Conclusions

Both concerted and stepwise mechanisms were identified by means of cyclic voltammetry in the investigated series of α-substituted acetophenones. In the stepwise cases, the cleavage rates and the standard potentials for the formation of the anion radical were derived from peak potential and peak width data. With the help of thermodynamical parameters obtained from the present study and from literature data, it was possible to identify and estimate the parameters that govern the concerted−stepwise dichotomy.

With acetophenones that do not bear electron withdrawing ring substituents, the two main governing factors are the bond dissociation energy and the oxidability of the leaving group. With only one exception, the latter parameter is largely predominant. It may even reverse an opposing effect of the bond dissociation energy. The same is true for compounds where the cleavage of the anion radical is so slow that it is overrun by dimerization. α-Substituted acetophenones thus provide several striking examples of the role of the oxidability of the leaving group as a mechanism controlling parameter.

The fluoro-substituent provides a converse example where the strength of the bond is so large that it overcompensates the unfavorable effect of the oxidability of F^-.

With electron withdrawing para-substituents such as, NO_2 and CN, the passage to a stepwise mechanism or the formation of a noncleaving anion radical is the result of a decrease in the LUMO energy.

With compounds following the stepwise mechanism, solvent reorganization appears in most cases as the major contributor to the intrinsic barrier of the cleavage reaction. It arises from the transfer of the negative charge initially located on the carbonyl oxygen to the leaving group. In this case too the fluoro compound exhibits a particular behavior. Not only is the solvent reorganization energy bigger, owing to the small size of the fluoride ion, but also the strength of the C−F is such that intramolecular reorganization is also much larger than with the other compounds.

It is also worth noting, that in the three cases where a concerted mechanism was identified, the lifetime of the anion radical is clearly larger than the time of a vibration. The concerted character of the reaction thus results from an energetic advantage rather than from the "nonexistence" of the anion radical intermediate.

Experimental Section

Chemicals. *N*,*N*′-Dimethylformamide (Fluka puriss absolute) and the supporting electrolyte *n*-Bu_4NBF_4 (Fluka puriss) were used as received. Phenacyl chloride and bromide were used as supplied by Aldrich, Lancaster, or Maybridge Chemical Co. **3** was prepared as described in ref 24. Phenacyl benzoates (**4a**, **4b**, and **4c**) were obtained according to literature procedure[25] from the corresponding phenacyl bromides and benzoic acid in the presence of triethylamine. Phenoxy derivatives (**5a**, **5b**) were synthesized, under phase-transfer-catalyzed conditions,[26a] from the reaction between a phenacyl bromide and m-cresol in presence of sodium hydroxide.[26b] Phenacyl sulfides (**7a**, **7b**) were prepared by reacting phenacyl bromide with the sodium salt of the appropriate thiol. **7b** was obtained under the same catalytic conditions[26a] as the phenoxy derivatives.

α-(Benzoyloxy)acetophenone 4a: mp 118 °C; IR ($CHCl_3$) 1725, 1705 cm^{-1}; NMR ($CDCl_3$) δ 5.45 (s, 2H), 7.20−8.15 (10H).

α-(Benzoyloxy)-*p*-nitroacetophenone 4b: mp 140 °C; IR 1725, 1710 cm^{-1}; NMR δ 5.50 (s, 2H), 7.20−8.35 (9H).

α-(*m*-Methylphenoxy)acetophenone 5a: mp 70 °C; IR 1690 cm^{-1}; NMR δ 5.15 (s, 2H), 6.75−8.00 (9H).

α-(*m*-Methylphenoxy)-*p*-methylacetophenone 5b: mp 68 °C; IR 1685 cm^{-1}; NMR δ 5.15 (s, 2H), 6.75−7.90 (8H).

Cyclic Voltammetry. The electrodes were carefully polished and ultrasonically rinsed with ethanol before each voltammogram. The ultramicroelectrodes were built from a gold wire (10 and 25 μm diameter) by using a reported procedure.[27] The counter-electrode was a platinum wire and the reference electrode an aqueous SCE electrode. The potentiostat, equipped with a positive feedback compensation and current measurer, used from 0.1 V/s until 500 V/s was the same as previously described.[28a] The instrument used with ultramicroelectrodes at high scan rates has been described elsewhere.[28b] The cyclic voltammetry experiments were carried out at 20 °C using a cell equipped with a double-wall jacket allowing circulation of water. At low temperature, the cell was thermostated by an isopropyl alcohol circulation and the reference electrode was maintained at 20 °C (the bridge containing the reference electrode was equipped with a double-wall jacket allowing circulation of water).

Supporting Information Available: Equations representing the construction of the diagrams of Figure 1 and figures of reversible cyclic voltammograms, cyclic voltammetric peak characteristics, and theoretical variations of E_p and $E_{p/2} - E_p$ with log ν (5 pages). See any current masthead page for ordering and Internet access instructions.

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