

# Estimation of Reduction and Standard Potentials of Acyl Radicals

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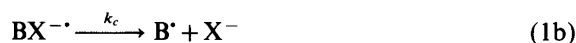
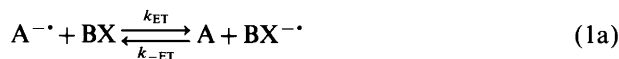
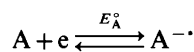
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Acyl radicals are formed in the electron transfer reaction between electrogenerated anion radicals of aromatic or heteroaromatic compounds and acid chlorides or anhydrides. A method based on the steady-state properties of the rotating disk electrode allows the determination of a dimensionless parameter  $q$ , which represents the competition between the reactions of coupling and reduction that the acyl radical can undergo with the aromatic anion radicals. Both reactions are fast compared with the decarbonylation of the acyl radical. From the measurement of  $q$  it is possible to extract the reduction potential  $E_{1/2}^q$ , the standard potential  $E_R^\circ$ , and the self-exchange reorganization energy  $\lambda_R(0)$  of the radicals investigated. The standard potentials of aliphatic acyl radicals are between  $-1.68$  and  $-1.75$  V vs. SCE. The corresponding values for the aromatic radicals are much more positive (between  $-1.02$  and  $-1.16$  V vs. SCE). In all cases the self-exchange reorganization energy  $\lambda_R(0)$  was found to be  $30 \text{ kcal mol}^{-1}$ .

In general little is known about the thermodynamics of radicals owing to their extremely high reactivity, but in recent years some groups have developed different methods for estimating their redox properties. Wayner and Griller have measured the reduction and oxidation potentials of some photochemically generated benzyl and substituted alkyl radicals by voltammetric detection.<sup>1</sup> A similar method for alkyl and hydroxyalkyl radicals has been applied by Benderskii and Krivenko.<sup>2</sup> Savéant *et al.* have estimated reduction potentials, standard potentials and self-exchange reorganization energies of butyl radicals by comparing the experimental linear sweep voltammograms of the corresponding butyl iodides or bromides with simulations.<sup>3</sup>

We have studied the competition between coupling and reduction in the reaction of electrogenerated aromatic anion radicals with radicals in order to determine the relevant potentials and the self-exchange reorganization energy. Previously different kinds of benzyl, allyl, sterically hindered and non-conjugated alkyl radicals have been investigated.<sup>4–6</sup> In this paper we report the results concerning the redox properties of acyl radicals about which very little is known in the literature.

Acyl radicals can be generated, e.g., chemically or electrochemically, by reduction of acid chlorides<sup>7</sup> or anhydrides<sup>8</sup> and by hydrogen abstraction from aldehydes.<sup>8,9</sup> In the indirect electrochemical reduction of acyl chlorides and anhydrides (BX) by aromatic anion radicals ( $A^-$ ),<sup>10</sup> the mechanism can be described by eqns. (1)–(3). The products  $AB^-$  and  $B^-$  will be



protonated by the supporting electrolyte or residual water or react with the substrate in a nucleophilic reaction. Side reactions such as H-atom abstraction and disproportionation of the acyl radicals are slow compared with reactions (2) and (3) and can be neglected.

For all alkyl halides and most benzyl halides the cleavage reaction (1b) has been shown to be concerted with the first electron transfer (ET) reaction [eqn. (1)].<sup>11</sup> From a qualitative point of view such a dissociative process seems more unlikely for, e.g., benzoic anhydride and benzoyl chloride, which have the possibility to accommodate an extra electron in their  $\pi$ -electron system. In our group, preliminary measurements of the transfer coefficient  $\alpha$  in the direct electrochemical reduction of these substrates are in agreement with a non-dissociative process ( $\alpha \approx 0.6$ ). However, the rate constant  $k_c$  for the cleavage reaction must be rather high ( $> 10^6 \text{ s}^{-1}$ ). In fast cyclic voltammetry using scan rates in the  $\text{kV s}^{-1}$  range with ultramicroelectrodes, it was not possible to detect the radical anion  $BX^-$ . Neither the value of  $k_c$  nor a

possible inner-sphere component in the ET reaction (1a) will influence the competition between reactions (2) and (3).

The rate constant  $k_2$  is probably near the diffusion-controlled limit, since the coupling reaction (2) is without charge repulsion. In the reaction between  $A^{\cdot-}$  and alkyl radicals,  $k_2$  has been measured by the use of radical clocks to be ca.  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>12</sup> This value is also assumed to be valid for all the coupling reactions in the present investigation. According to Marcus theory the rate constant  $k_3$  depends upon the reorganization energy for reaction (3) and the difference in standard potentials of the reactants.

Since the method and the theoretical background have already been described in detail,<sup>6</sup> only a short description of it will be given here. The dimensionless parameter  $q = k_3/(k_2 + k_3)$  represents the competition between coupling [eqn. (2)] and reduction [eqn. (3)]. If the anion radical couples with  $B^{\cdot}$  ( $k_3 \ll k_2$ ),  $q$  is equal to 0; if  $B^{\cdot}$  is reduced by the anion radical ( $k_3 > k_2$ ),  $q$  is near 1. When  $q$  is equal to 0.5 ( $k_3 = k_2$ ) the corresponding standard potential of the anion radical can be considered as the reduction potential of the radical  $B^{\cdot}(E_{1/2}^q)$ . In practice it is found by interpolation in a plot of  $q$  versus the standard potentials  $E_A^\circ$  of a series of mediators. The  $q$ -values can be determined by means of linear sweep voltammetry (LSV), chronoamperometry, coulometry and the rotating disk electrode (RDE) technique. With the knowledge of  $k_2$ , the reorganization energy  $\lambda$  for reaction (3) and  $E_{1/2}^q$ , it is possible to calculate  $E_R^\circ$ , the standard potential of the radical [eqns. (4) and (5)]. The parameter  $A$  is taken

$$E_R^\circ = E_{1/2}^q + H_{\text{corr}} \quad (4)$$

$$H_{\text{corr}} = \frac{\lambda}{F} \left\{ 1 - \left( \frac{4RT}{\lambda} \ln \left[ \frac{(k_d/k_2) - 1}{A} \right] \right)^{1/2} \right\} \quad (5)$$

equal to 0.2, and the diffusion rate constant  $k_d$  to  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . The reorganization energy  $\lambda$  can be estimated from the width of the  $q$  vs.  $E_A^\circ$  plot (S-shaped curve) by comparison with calculated curves.

From the value of  $\lambda$  it is possible to determine the self-exchange reorganization energy of the radical  $\lambda_R(0)$  using the Marcus cross relation [eqn. (6)]. The parameter

$$\lambda = 1/2 [\lambda_{A^{\cdot-}}(0) + \lambda_R(0)] \quad (6)$$

$\lambda_{A^{\cdot-}}(0)$  is the self-exchange reorganization energy for the electron donor. For most aromatic anion radicals it has been measured equal to ca.  $10 \text{ kcal mol}^{-1}$  by EPR spectroscopy.<sup>13</sup> The reaction between aromatic anion radicals and an acceptor including the parent aromatic compound has been suggested<sup>14</sup> not to be a pure outer-sphere ET, but to have an inner-sphere component with a stabilization energy in the order of  $3\text{--}7 \text{ kcal mol}^{-1}$ . This would influence the determination of the reorganization energy  $\lambda$  and the potentials (probably by several hundred millivolts). The suggestion, however, has been questioned;<sup>15</sup> we are therefore still treating our data with the

assumption that aromatic anion radicals are outer-sphere electron donors until convincing evidence of inner-sphere ET for this reaction is presented. The value of  $10 \text{ kcal mol}^{-1}$  for  $\lambda_{A^{\cdot-}}(0)$  will be used in the following.

Acid chlorides and anhydrides, in contrast with alkyl halides, are often adsorbed onto the working electrode and are easily hydrolysed by traces of water, always present even in the most carefully dried *N,N*-dimethylformamide (DMF). LSV and chronoamperometry, which have been the methods of choice for measuring  $q$ -values in the previous investigations,<sup>4-6</sup> could thus not be used in this case owing to the long duration of such experiments. Recently a new technique, based on the steady-state properties of the rotating disk electrode, has been developed.<sup>16</sup> In this method the anion radical is first generated by electrochemical reduction to a certain concentration ( $C_{A^{\cdot-}}$ ). A steady-state voltammogram is then recorded and a small amount of the BX compound is added ( $C_{\text{BX}} < 1/2 C_{A^{\cdot-}}$ ). When the substrate is consumed in the reaction with the anion radical (usually within a minute), another voltammogram is recorded and the  $q$ -value can be determined directly from the changes in the steady-state curves. Other advantages of this method compared with LSV and chronoamperometry are that the measurements are not affected by a direct reduction of the BX compound and can be used for slower reactions, allowing, in this way, in most cases the determination of  $q$  over the whole range. Furthermore the knowledge of the exact concentration of the BX compound is not necessary, and a nucleophilic substitution between  $AB^-$  or  $B^-$  and BX will not influence the measurements.

## Results and discussion

In this report the following acid chlorides and anhydrides have been investigated: acetic anhydride (1), acetyl chloride (2), succinic anhydride (3), phenylacetyl chloride (4), benzoic anhydride (5), benzoyl chloride (6), 4-methoxybenzoyl chloride (7), 3-methoxybenzoyl chloride (8), 4-chlorobenzoyl chloride (9), 4-cyanobenzoyl chloride (10) and 1-naphthoyl chloride (11). The substrates were chosen in order to examine the influence of some substituents on the reduction and standard potentials of acyl radicals.

The experimental  $q$ -values for the reaction between electrogenerated anion radicals and acid chlorides and anhydrides are presented in Table 1. The  $q$ -values for the acetyl and benzoyl radicals have been measured with both the acid chloride and the anhydride, and even though there are slight differences in the measurements, the reduction potentials agree within a few tenths of millivolts. These results indicate that the acid chlorides can be used without restrictions in spite of their higher reactivity towards hydrolysis and their reaction with DMF which leads to the formation of a small amount of an ionic adduct ( $\leq 3\%$ ).<sup>17</sup>

The values obtained for the reduction potential  $E_{1/2}^q$ , the standard potential  $E_R^\circ$  and the self-exchange

Table 1. Competition parameter ( $q$ ) for some anhydrides and acid chlorides in DMF/TBABF<sub>4</sub> measured by RDE. The uncertainty in  $q$  is  $\pm 0.05$ .

	BX	Mediator	$-E_A^\circ/V^a$	$q$
1	Acetic anhydride	Anthracene	1.890	0.00
		1,2-Benzanthracene	1.922	0.15
		Pyrene	2.018	0.50
		2,7-Di- <i>tert</i> -butylpyrene	2.074	0.60
		3-Methoxypyrene	2.081	0.70
		<i>p</i> -Terphenyl	2.250	0.85
2	Acetyl chloride	<i>p</i> -Tolunitrile	2.337	0.90
		9-Phenylanthracene	1.827	0.05
		Anthracene	1.890	0.10
		1,2-Benzanthracene	1.922	0.30
		Pyrene	2.018	0.70
		3-Methoxypyrene	2.081	0.75
3	Succinic anhydride	<i>m</i> -Tolunitrile	2.264	0.80
		9-Phenylanthracene	1.827	0.05
		Anthracene	1.890	0.10
		9,10-Dimethylanthracene	1.906	0.15
		Pyrene	2.018	0.45
		3-Methoxypyrene	2.081	0.50
4	Phenylacetyl chloride	Chrysene	2.182	0.75
		<i>p</i> -Terphenyl	2.250	0.95
		9-Phenylanthracene	1.827	0.10
		Anthracene	1.890	0.15
		9,10-Dimethylanthracene	1.906	0.40
		1,2-Benzanthracene	1.922	0.40
5	Benzoic anhydride	Pyrene	2.018	0.70
		3-Methoxypyrene	2.081	0.75
		Chrysene	2.182	0.90
		<i>m</i> -Tolunitrile	2.264	0.95
		4-Chloroazobenzene	1.183	0.05
		Azobenzene	1.279	0.15
6	Benzoyl chloride	2-Methoxyazobenzene	1.299	0.20
		1-Cyanoisoquinoline	1.435	0.65
		Perylene	1.613	0.80
		Fluoranthene	1.688	0.85
		Pyrene	2.018	0.90
		4-Chloroazobenzene	1.183	0.05
7	4-Methoxybenzoyl chloride	Azobenzene	1.279	0.15
		2-Methoxyazobenzene	1.299	0.15
		1-Cyanoisoquinoline	1.435	0.55
		Perylene	1.613	0.85
		Benzophenone	1.707	0.90
		Anthracene	1.890	0.95
8	3-Methoxybenzoyl chloride	3-Chloroazobenzene	1.135	0.00
		Azobenzene	1.279	0.15
		2,4-Dimethoxyazobenzene	1.416	0.40
		1-Cyanoisoquinoline	1.435	0.55
		Acenaphthylene	1.590	0.80
		Perylene	1.613	0.85
9	4-Chlorobenzoyl chloride	Fluoranthene	1.688	0.95
		3-Chloroazobenzene	1.135	0.10
		4-Chloroazobenzene	1.183	0.20
		Azobenzene	1.279	0.30
		2-Methoxyazobenzene	1.299	0.30
		1,4-Diacetylbenzene	1.407	0.80
10	4-Cyanobenzoyl chloride	1-Cyanoisoquinoline	1.435	0.85
		Perylene	1.613	0.90
		<i>p</i> -Methoxycarbonyl-azobenzene	1.015	0.10
		3-Chloroazobenzene	1.135	0.15
		4-Chloroazobenzene	1.183	0.15
		Azobenzene	1.279	0.40
11	1-Naphthoyl chloride	2-Methoxyazobenzene	1.299	0.45
		1-Cyanoisoquinoline	1.435	0.80
		Perylene	1.613	0.95
		3-Chloroazobenzene	1.135	0.05
		Azobenzene	1.279	0.25
		2,4-Dimethoxyazobenzene	1.416	0.40
		1-Cyanoisoquinoline	1.435	0.80
		Methyl <i>p</i> -cyanobenzoate	1.536	0.90
		Acenaphthylene	1.590	1.00

<sup>a</sup>Vs. SCE.

reorganization energy  $\lambda_{\text{R}}(0)$  of the acyl radicals are presented in Table 2. The  $E_{1/2}^q$  and  $E_{\text{R}}^{\circ}$  of the aliphatic acyl radicals (compounds 1–4) are similar to those previously measured for the non-conjugated alkyl radicals,<sup>5,6</sup> while the corresponding values for the aromatic acyl radicals (compounds 5–11) are much more positive (ca. 600–700 mV) and in the same potential region as the benzyl radicals.<sup>4</sup> This may, at first sight, seem somewhat surprising since all the acyl radicals are regarded to be of the  $\sigma$  type,<sup>8,9,18,19</sup> where the unpaired electron is located in an  $sp^2$ -like orbital on the carbonyl carbon atom.<sup>8</sup> The stabilization of the radicals arises mainly by conjugation with the lone pair of the oxygen atom in the carbonyl group and it is thus rather unaffected by the presence of adjacent substituents, which is confirmed by several results in the literature. For instance, replacement of a hydrogen atom in formaldehyde, e.g., by a methyl, vinyl or phenyl group, shows no effect on the aldehydic C–H bond strength,<sup>20,21</sup> while it has a large influence on the C–H bond strength of methane.<sup>22</sup> Similarly the major hyperfine splitting in the EPR spectrum of the benzoyl radical is due to the *meta* hydrogen atoms<sup>9</sup> and not to the *para* hydrogen as in the benzyl  $\pi$ -radical.<sup>23</sup>

Evidently, there are factors other than radical stabilization to consider in order to explain the results obtained for the aromatic acyl radicals: the stability of the corresponding anions and the change of structure and hybridization on going from radical to anion. A molecular orbital examination has been performed on some carbonyl anions in the gas phase in order to characterize their thermodynamic stability.<sup>24</sup> The anions are, in general,  $sp^2$ -hybridized except for the benzoyl anion which is nearly linear. The bond between the carbonyl carbon and the adjacent carbon has some double bond character only in the latter case. The presence of the phenyl group allows extensive delocalization of the negative charge, which is not possible in the simple aliphatic acyl anions. It thus seems likely that the main reason for the much more positive reduction and standard potentials of the aromatic acyl radicals can, in general, be

attributed to the stabilizing effect of the aryl group on the corresponding anion.

The introduction of a phenyl group on the acetyl radical (compound 4) has, as expected, a slight effect on  $E_{1/2}^q$  and  $E_{\text{R}}^{\circ}$  in a positive direction. The results obtained for the substituted benzoyl radicals indicate that the presence of a methoxy group (compounds 7, 8) does not have an appreciable influence on the potentials of the benzoyl radical, regardless of the position of the substituent. In contrast, the presence of a chloro (compound 9) or a cyano group (compound 10), both in position 4, seems to make the potentials more positive by about 100 mV. At the moment it is difficult to give a satisfactory interpretation of these results and to explain why the substituents investigated have such different effects on the redox properties of the benzoyl radical. Theoretical calculations are in progress in order to establish the reliability of these observations.

The reorganization energy  $\lambda$  for reaction (3), estimated from the width of the  $q$  vs.  $E_{\text{A}}^{\circ}$  plot (Fig. 1), is equal to 20 kcal mol<sup>-1</sup> in all the cases. With the knowledge of  $\lambda$  and using an average value of  $k_2k_{\text{d}}^{-1}$  equal to 0.1,<sup>6</sup> the potential correction  $H_{\text{corr}}$  for transforming the reduction potential of the radical into the corresponding standard potential [eqn. (4)] could be calculated from eqn. (5) to be 280 mV. From eqn. (6) it follows that the self-exchange reorganization energy  $\lambda_{\text{R}}(0)$  for all the acyl radicals under investigation is equal to 30 kcal mol<sup>-1</sup>. This value is between that obtained for an alkyl radical (50 kcal mol<sup>-1</sup>)<sup>5,6</sup> and that for a benzyl or allyl radical (10 and 20 kcal mol<sup>-1</sup>, respectively).<sup>4,6</sup> The rather high  $\lambda_{\text{R}}(0)$  for an alkyl radical is a reflection of the large reorganization necessary to transform the flat (or nearly so) alkyl radical into the corresponding pyramidal carbanion. In the same way the small  $\lambda_{\text{R}}(0)$  value for the benzyl and allyl radicals indicates the similarity of the structures of the radical and anion.<sup>25</sup> A plausible explanation for the results obtained for the acyl radicals is thus that the reorganization of the radical structure, which occurs when the carbanions are formed, is large compared

Table 2. Reduction potentials  $E_{1/2}^q$ , standard potentials  $E_{\text{R}}^{\circ}$  and reorganization energies  $\lambda_{\text{R}}(0)$  for acyl radicals. The uncertainty in the determination of  $E_{1/2}^q$  and  $E_{\text{R}}^{\circ}$  is estimated to be  $\pm 50$  mV and  $\pm 150$  mV, respectively.<sup>6</sup> The uncertainty in  $\lambda_{\text{R}}(0)$  is  $\pm 10$  kcal mol<sup>-1</sup>.

	BX	$-E_{1/2}^q/\text{V}^a$	$-E_{\text{R}}^{\circ}/\text{V}^a$	$\lambda_{\text{R}}(0)/\text{kcal mol}^{-1}$
1	Acetic anhydride	2.03	1.75	30
2	Acetyl chloride	1.98	1.70	30
3	Succinic anhydride	2.03	1.75	30
4	Phenylacetyl chloride	1.96	1.68	30
5	Benzoic anhydride	1.41	1.13	30
6	Benzoyl chloride	1.42	1.14	30
7	4-Methoxybenzoyl chloride	1.44	1.16	30
8	3-Methoxybenzoyl chloride	1.43	1.15	30
9	4-Chlorobenzoyl chloride	1.30	1.02	30
10	4-Cyanobenzoyl chloride	1.30	1.02	30
11	1-Naphthoyl chloride	1.35	1.07	30

<sup>a</sup>Vs. SCE.

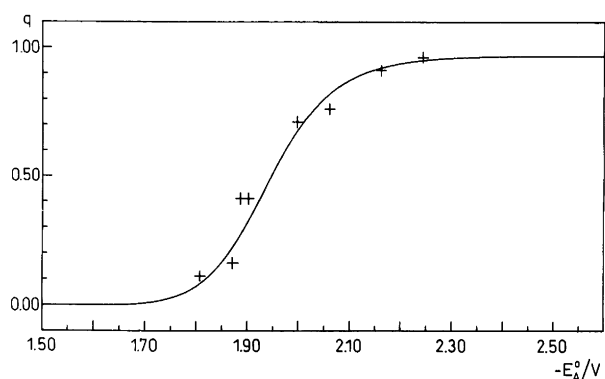


Fig. 1.  $q$ -Values of phenylacetyl chloride vs. the redox potential  $E_A^0$  (vs. SCE) of some aromatic mediators. The curve is calculated using  $E_{1/2}^q = -1.96$  V,  $k_2 k_d^{-1} = 0.05$  and  $\lambda = 20$  kcal mol $^{-1}$ .

with the benzyl system but smaller than in the alkyl system and rather like the allyl one. It is nevertheless surprising that the aliphatic and aromatic acyl radicals have been found to have the same reorganization energies, considering that the structure of the corresponding anions are very different from each other.<sup>24</sup>

The normal polarization of the carbonyl group and the ease of formation of the carbonyl cation suggest that a negative charge on the carbonyl carbon atom is not very favourable, even though the structure of the carbonyl anion should present some stabilization due to the  $sp^2$  hybridization and to the inductive effect of the electronegative oxygen atom.<sup>24</sup> Carbonyl anions have generally been considered to be 'inaccessible' from a synthetic point of view until recently. The most common way to approach this kind of anion has been the synthesis of 'acyl anion equivalents', which can be regarded as masked nucleophilic acylating agents. They are used to reverse the typical reactivity of the carbonyl group from electrophilic to nucleophilic ('umpolung').<sup>26</sup> Seyferth *et al.* have recently investigated the reaction between carbon monoxide and an alkyllithium at low temperature ( $-110^\circ\text{C}$ ), using a mixture of tetrahydrofuran, diethyl ether and pentane as the solvent.<sup>27</sup> The acyllithium reagent formed in this way can be used to perform direct nucleophilic acylation on different kinds of organic electrophile. Some non-enolizable aldehydes as trimethylacetaldehyde undergo a deprotonation with lithium tetramethylpiperidide in tetrahydrofuran at  $-78^\circ\text{C}$  generating with ease an acyllithium species which can react in a nucleophilic way with the aldehyde.<sup>28</sup> These are just few examples which show the synthetic possibilities of such reactive intermediates, and which suggest some potential applications of electrochemically generated acyl anions.

Electrolytic reduction of some activated olefins such as, e.g., ethyl cinnamate in the presence of acetic anhydride or acetyl chloride resulted in the addition of an acyl group to the double bond in the  $\beta$  position to the activating group.<sup>29,30</sup> The standard potential of ethyl cinnamate is  $-1.82$  V vs. SCE and the reduction potential of the acetyl

radical is ca.  $-2.00$  V vs. SCE (Table 2), so a radical coupling seems the most likely reaction route. Addition of two electrons and a proton to the double bond followed by acylation of the resulting carbanion would give acylation at the carbon  $\alpha$  to the ester group, and such a reaction route can be disregarded.

Electrochemical reduction of azobenzene in the presence of the succinyl chloride gave 1,2-diphenylpyridazine-3,6-dione in fair yield. The mechanism of the first acylation is probably analogous to that of activated olefins, whereas the ring closure undoubtedly is a direct acylation of the monoacylated hydrazobenzene anion.<sup>31</sup>

A possible mechanistic complication in the investigation of acyl radicals is that they may decarbonylate giving rise to several kinds of side reaction. The decarbonylation rate constant  $k_{\text{dec}}$  varies for the different acyl radicals in the following order: benzyl/allyl > tertiary > secondary  $\gg$  primary  $\gg$  aryl.<sup>32</sup> For the propanoyl and similar radicals  $k_{\text{dec}}$  is in the range  $250$ – $500$  s $^{-1}$  at  $25^\circ\text{C}$ ,<sup>32</sup> and the decarbonylation process can be neglected. Among the radicals investigated, the fastest decarbonylation is undergone by the phenylacetyl radical with a  $k_{\text{dec}}$  equal to  $5.05 \times 10^6$  s $^{-1}$  at  $18^\circ\text{C}$  in THF,<sup>33</sup> and in this case some complications are possible in the measurements of  $q$ .

If the anion radical concentration  $C_{A^{\cdot-}}$  in the RDE method is assumed to be constant ( $C_{\text{BX}} \ll C_{A^{\cdot-}}$ ) throughout the whole experiment, the importance of the decarbonylation process can be estimated from expression (7).

$$\frac{k_{\text{dec}}}{(k_2 + k_3) C_{A^{\cdot-}} + k_{\text{dec}}} \quad (7)$$

In the experiments with phenylacetyl chloride the initial concentrations of  $A^{\cdot-}$  were kept higher ( $\approx 30$  mM) than normal ( $\approx 10$  mM), while  $C_{\text{BX}}$  as always was in the order of  $2$ – $4$  mM. If  $(k_2 + k_3)$  is assumed to be ca.  $10^9$  M $^{-1}$  s $^{-1}$  the extent of the phenylacetyl radical following the decarbonylation route is about 15%. When the importance of the catalytic mechanism increases,  $(k_2 + k_3)$  is higher than  $10^9$  M $^{-1}$  s $^{-1}$  and the percentage should be smaller. Some RDE experiments were carried out with a lower concentration of  $A^{\cdot-}$  ( $10$ – $15$  mM) in order to reveal the possible effect of the decarbonylation process on the  $q$ -values. The results were exactly the same as previously obtained and it does not seem probable that the latter process is a serious competitive side reaction for any of the radicals investigated. Furthermore, in a preparative experiment performed with anthracene and phenylacetyl chloride, the analysis of the reduction mixture by means of GC-MS showed only the formation of the corresponding coupling compound. Toluene, which could be formed by indirect reduction of the benzyl radical,<sup>4</sup> generated from the phenylacetyl radical by loss of the carbonyl group, was not detected.

Some preparative reductions and analyses of the catholyte in the RDE experiments were performed with acetic and benzoic anhydrides, in order to confirm the

formation of coupling products ( $q=0$ ) and reduction products ( $q \approx 0.9$ ). In contrast with the RDE experiments the BX compound was always in excess (2–5) in the preparative ones.

The preparative reduction of anthracene in the presence of acetic anhydride ( $q=0$ ) has already been investigated and the coupling compound isolated and characterized.<sup>10</sup> The preparative experiment with *p*-terphenyl and acetic anhydride ( $q=0.85$ ) was analysed by gas-chromatography. The only reaction product found was acetaldehyde formed by protonation of the acetyl anion produced in reaction (3). Formation of acetaldehyde from an H-atom abstraction process by the acetyl radical is not likely. The rate constant for H-atom abstraction by acyl radicals from, e.g., hexane has been estimated to have rather small values at room temperature ( $\leq 5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>34</sup> and from  $\text{Bu}_3\text{SnH}$  the rate constant is much smaller than that for H-abstraction by alkyl radicals.<sup>7e</sup> Diacetyl was not detected; evidently, the protonation is faster than the nucleophilic reaction between the acetyl anion and acetic anhydride.

In the preparative and RDE-experiments with perylene and benzoic anhydride ( $q=0.80$ ) benzaldehyde was detected by GC analysis. Contrary to what is found in the direct cathodic reduction of benzoyl chloride,<sup>7a</sup> formation of the more easily reducible benzil (and its reduction products) did not occur, which was also confirmed by cyclic voltammograms recorded during the RDE experiment. In the preparative reduction with azobenzene and benzoic anhydride ( $q=0.15$ ) the isolated coupling compound was identified as *N,N'*-dibenzoylhydrazobenzene. The formation of this product can be attributed to a nucleophilic substitution by the  $\text{AB}^-$  species, formed in reaction (2), on the benzoic anhydride present in excess, similarly to the reaction product from the reduction of azobenzene in the presence of the succinyl chloride<sup>31</sup> and of anthracene in the presence of acetic anhydride.<sup>10</sup>

## Experimental

**Materials.** The mediators were the same as used previously.<sup>4–6</sup> Acetic anhydride, acetyl chloride, succinic anhydride, phenylacetyl chloride, benzoyl chloride and 4-chlorobenzoyl chloride were obtained commercially and distilled or recrystallized before use. The other substrates were prepared by conventional methods. The supporting electrolyte,  $\text{Bu}_4\text{NBF}_4$ , and the solvent, *N,N*-dimethylformamide, were purified by standard procedures. The electrolyte solution was dried through a column of activated alumina just before each experiment.

**Equipment.** The instrumentation has been described previously.<sup>35</sup> The cells and the electrodes were of conventional type.

**Procedures.** The parameter  $q$  estimated with the RDE method described in detail elsewhere<sup>16</sup> was calculated from eqn. (8).

$$q = 2 \left( \frac{D_{\text{A}^{\cdot-}}}{D_{\text{A}}} \right)^{2/3} \left( \frac{\Delta i_{\text{A}}}{\Delta i_{\text{A}^{\cdot-}}} \right) - 1 \quad (8)$$

The ratio between the diffusion coefficients of the anion radical and the aromatic compound ( $D_{\text{A}^{\cdot-}}/D_{\text{A}}$ ) was determined by the method described in Ref. 16. The parameters  $\Delta i_{\text{A}}$  and  $\Delta i_{\text{A}^{\cdot-}}$  are the changes in the reduction and oxidation currents in the steady-state voltammograms recorded before and after addition of BX. The initial concentration of  $\text{A}^{\cdot-}$  was normally ca. 10 mM and the concentration of BX was 2–4 mM. All the experiments were carried out in DMF using  $\text{Bu}_4\text{NBF}_4$  as the supporting electrolyte at room temperature.

In the preparative reduction of azobenzene in the presence of benzoic anhydride the electron consumption was equal to 1.9 and *N,N'*-dibenzoylhydrazobenzene was isolated and characterized: m.p. 159–161°C (lit.<sup>36</sup> 161–162°C); <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  7.0–7.65 (m, aromatic protons); IR (KBr):  $\nu$  1680, 1660, 1600, 1500, 1440, 1310, 1280  $\text{cm}^{-1}$ ; MS [IP 70 eV,  $m/z$ , (%): 392 (30), 287 (10), 197 (10), 105 (100), 77 (30)]. The coupling compound formed in the reaction between anthracene anion radical and acetic anhydride has been described.<sup>10</sup>

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## References

- Wayner, D. D. M., McPhee, D. J. and Griller, D. *J. Am. Chem. Soc.* 110 (1988) 132; Sim, B. A., Griller, D. and Wayner, D. D. M. *J. Am. Chem. Soc.* 111 (1989) 754; Milne, P. H., Wayner, D. D., DeCosta, D. P. and Pincock, J. A. *Can. J. Chem.* 70 (1992) 121.
- Benderskii, V. A. and Krivenko, A. G. *Russ. Chem. Rev.* 59 (1990) 1.
- Andrieux, C. P., Gallardo, I. and Savéant, J.-M. *J. Am. Chem. Soc.* 111 (1989) 1620.
- Fuhlendorff, R., Occhialini, D., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* 43 (1989) 803.
- Occhialini, D., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* 44 (1990) 715.
- Occhialini, D., Kristensen, J. S., Daasbjerg, K. and Lund, H. *Acta Chem. Scand.* 46 (1992) 474.
- (a) Guirado, A., Barba, F., Manzanera, C. and Velasco, M. *D. J. Org. Chem.* 47 (1982) 142; (b) Arthur, P. and Lyons, H. *Anal. Chem.* 24 (1952) 1422; (c) Guirado, A., Barba, F. and Martin, J. *Synth. Commun.* 13 (1983) 327; (d) Guirado, A., Barba, F. and Martin, J. *Electrochim. Acta* 29 (1984) 587; (e) Luszyk, J., Luszyk, E., Maillard, B. and Ingold, K. U. *J. Am. Chem. Soc.* 106 (1984) 2923; (f) Urove, G. A. and Peters, D. G. *J. Org. Chem.* 58 (1993) 1620.
- Bennett, J. E. and Mile, B. *Trans. Faraday Soc.* 67 (1971) 1587.
- Krusic, P. J. and Rettig, T. A. *J. Am. Chem. Soc.* 92 (1970) 722.
- Lund, H. *Acta Chem. Scand., Ser. B* 31 (1977) 424.
- Andrieux, C. P., Gallardo, I., Savéant, J.-M. and Su, K. B. *J. Am. Chem. Soc.* 108 (1986) 638; Andrieux, C. P., Savéant, J.-M. and Su, K. B. *J. Phys. Chem.* 90 (1986) 3815.

12. Pedersen, S. U. and Lund, T. *Acta Chem. Scand.* **45** (1991) 397.
13. Larsen, H., Pedersen, S. U., Pedersen, J. A. and Lund, H. *J. Electroanal. Chem.* **331** (1992) 971.
14. Ebersohn, L. and Shaik, S. S. *J. Am. Chem. Soc.* **112** (1990) 4484.
15. Savéant, J.-M. *J. Am. Chem. Soc.* **114** (1992) 10595, footnote 12.
16. Daasbjerg, K. *Acta Chem. Scand.* **47** (1993) 398.
17. Hall, H. K. Jr. *J. Am. Chem. Soc.* **78** (1956) 2717.
18. Caronna, T., Fronza, G., Minisci, F., Porta, O. and Gardini, G. P. *J. Chem. Soc. Perkin Trans. 2* (1972) 1477.
19. Minisci, F. *Top. Curr. Chem.* **62** (1976) 1.
20. Solly, R. K. and Benson, S. W. *J. Am. Chem. Soc.* **93** (1971) 1592.
21. Alfassi, Z. B. and Golden, D. M. *J. Am. Chem. Soc.* **95** (1973) 319.
22. Benson, S. W. *J. Chem. Educ.* **42** (1965) 502.
23. Dixon, W. T. and Norman, R. O. C. *J. Chem. Soc.* (1964) 4857.
24. Chandrasekhar, J., Andrade, J. G. and Schleyer, P. v. R. *J. Am. Chem. Soc.* **103** (1981) 5612.
25. Mikkelsen, K. V., Pedersen, S. U., Lund, H. and Swanström, P. *J. Phys. Chem.* **95** (1991) 8892.
26. Seebach, D. and Corey, E. J. *J. Org. Chem.* **40** (1975) 231; Seebach, D. *Synthesis* (1969) 17; Oakes, F. T. and Sebastian, J. F. *J. Org. Chem.* **45** (1980) 4959; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **8** (1969) 639.
27. Seyferth, D. and Hui, R. C. *J. Am. Chem. Soc.* **107** (1985) 4551.
28. Shiner, C. S., Berks, A. H. and Fisher, A. M. *J. Am. Chem. Soc.* **110** (1988) 957.
29. Lund, H. and Degrand, C. *Tetrahedron Lett.* (1977) 3593; *Acta Chem. Scand., Ser. B* **33** (1979) 57.
30. Shono, T., Nishiguchi, I. and Ohmizu, H. *Chem. Lett.* (1977) 1021; *J. Am. Chem. Soc.* **99** (1977) 7396.
31. Degrand, C., Grosdemouge, C. and Compagnon, P.-L. *Tetrahedron Lett.* (1978) 3023; Degrand, C. and Jacquin, D. *Tetrahedron Lett.* (1978) 4955; Degrand, C., Compagnon, P.-L., Belot, G. and Jacquin, D. *J. Org. Chem.* **45** (1980) 1189.
32. Boger, D. L. and Mathvink, R. J. *J. Org. Chem.* **57** (1992) 1429.
33. Lunazzi, L., Ingold, K. U. and Scaiano, J. C. *J. Phys. Chem.* **87** (1983) 529.
34. Neville, A. G., Brown, C. E., Rayner, D. M., Luszyk, J. and Ingold, K. U. *J. Am. Chem. Soc.* **113** (1991) 1869.
35. Pedersen, S. U. *Acta Chem. Scand., Ser. A* **41** (1987) 391.
36. Freundler, P. *C. R. Acad. Sci. Paris, Ser. C* **136** (1903) 1553.

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