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Quantitative Evaluation of the Mechanism of Electroreduction of Benzoyl Cyanides

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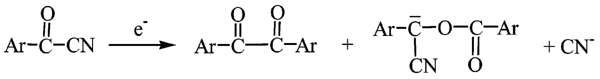
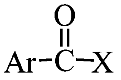


The mechanism of reduction of benzoyl cyanide, **6**, *p*-methoxybenzoyl cyanide, **7**, and *p*-chlorobenzoyl cyanide, **8**, has been studied in acetonitrile (**6** and **7**), *N*,*N*-dimethylformamide (**6**), and acetonitrile containing water (all three compounds). The reaction proceeds by initial reduction to form the anion radical followed by dimerization to produce an intermediate dianion, the dianion of the dicyanohydrin of benzil. The latter loses cyanide to give the anion of the monocyanohydrin of benzil, which undergoes two parallel reactions: expulsion of cyanide to give the corresponding benzil and rearrangement to the monoanion of mandelonitrile benzoate. The addition of water brings about an increase in the dimerization rate constant and an associated increase in the amount of benzil that is produced. The standard potentials for the initial reduction step have been evaluated, and their dependence on the substituent is discussed. The dimerization rate constants have also been evaluated.

Introduction

There are many examples in which removal from or addition of an electron to a neutral molecule will result in labilization of a given bond that allows a bond-cleavage reaction to occur.[1] In the case of reduction reactions, the bond cleavage can be concerted with electron transfer, as in the reduction of alkyl chlorides, bromides, and iodides. In most cases, however, the anion radical exists as a true intermediate with the rate of bond cleavage varying from very large (some aryl halides) to quite small (nitroalkanes).[1]

A number of classes of compounds contain an acyl function as in **1**. When X = Cl, the intermediate anion radical is short-lived and the acyl radical formed by cleavage of chloride gives a number of products, often via coupling to form benzils that are subsequently reduced.[2−8] The same type of reaction occurs when X = ArC(O)O, where the cleavage reaction gives aryloate ion and acyl radical with some of the latter dimerizing to give a benzil derivative.[9−11] There is a possibility that the benzil compounds are formed by prior dimerization of the anion radicals, followed by cleavage of the X substituent. Such is definitely the case when methyl benzoate (X = OCH_3) is reduced in the presence of magnesium ions, which promote the dimerization. The resulting dimer expels methoxide to produce benzil.[12] Therefore, the timing of the bond cleavage is variable. It occurs sometimes in the anion radical and sometimes after dimerization. A reaction analogous to the dimerization pathway has been reported for some diesters for which, depending on structure, the dianion diradicals undergo cyclization with expulsion of alkoxide giving benzil.[13]



$$\mathrm{Ar{-}\overset{\overset{O}{\|}}{C}{-}X}$$

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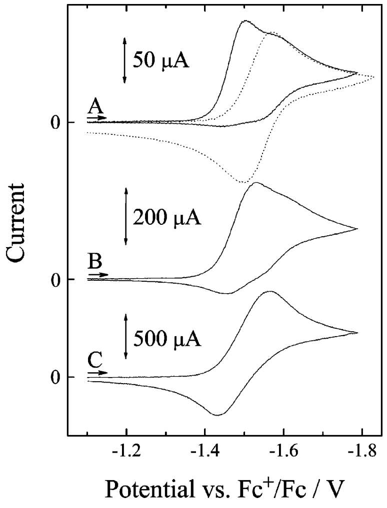
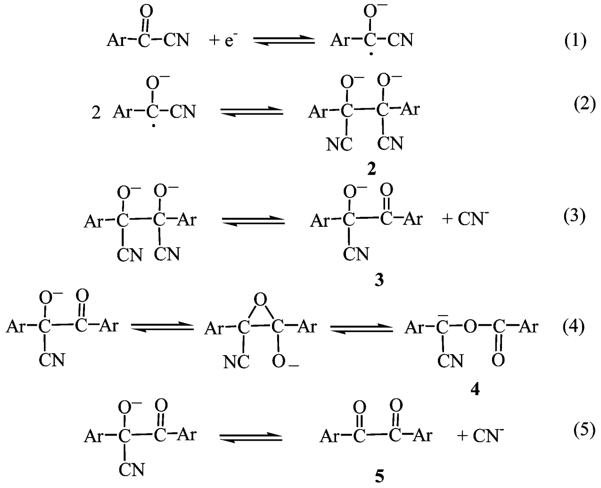


FIGURE 1. Voltammograms of 2.40 mM benzoyl cyanide, **6**, obtained in acetonitrile. (A) 0.20, (B) 2.00, and (C) 20.0 V/s. Dotted curve in A is for 2.00 mM benzil, also at 0.20 V/s.

Interesting results have been obtained for the reduction of benzoyl cyanides, X = CN,[14] wherein references to chemical reductions and their importance may be found. Preparative-scale reduction in either acetonitrile or acetonitrile/water (82.5% acetonitrile, v/v) gave principally, after workup, the corresponding mandelonitrile benzoate in the former and the corresponding benzil, **5**, in the latter mixed solvent. The results were interpreted in terms of the following reaction scheme.



The key step in this scheme is the dimerization of the initially formed anion radicals to form intermediate dianion **2**. Protonation of **2** gives the benzil dicyanohydrin, which sometimes precipitated in the partially aqueous medium, thus protecting the benzil from further reduction.[14] In the absence of added water, the principal product is apparently the anion of the mandelonitrile benzoate, **4**, which is protonated during workup to give mandelonitrile benzoate, the product that was isolated.[14] Thus, the products are well established but no detailed study of the mechanism of reduction of this type of compound has been reported.

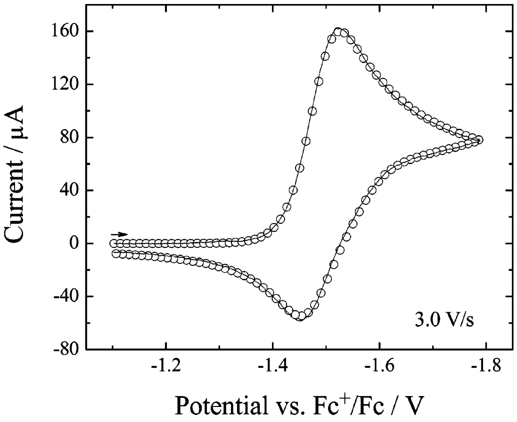


FIGURE 2. Voltammogram of 0.92 mM benzoyl cyanide, **6**, in acetonitrile. Curve: background-corrected voltammogram. Points: simulation.

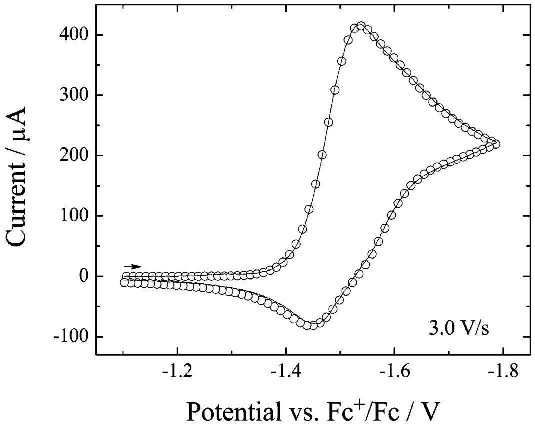


FIGURE 3. Voltammogram of 2.40 mM benzoyl cyanide, **6**, in acetonitrile.

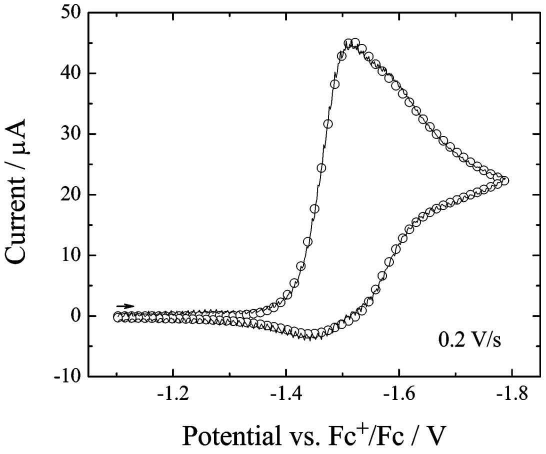


FIGURE 4. Voltammogram of 0.92 mM benzoyl cyanide, **6**, in acetonitrile.

In this article, we report on a mechanistic study of the reduction of three benzoyl cyanides (p-X−$C_6H_4C(O)CN$ with X = H, Cl, and OCH_3) in which we evaluated thermodynamic and kinetic parameters in the mechanism. We demonstrate that the reaction proceeds by initial formation of the anion radical followed by dimerization to produce the dimeric dianion, **2**. This dimeric dianion undergoes bond cleavage to give cyanide and the anion of the monocyanohydrin of the benzil, **3**. The latter

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TABLE 1. Experimental Conditions and Simulation Parameters for Benzoyl Cyanide, 6, in Acetonitrile (Upper Part of the Table) and Dimethylformamide (Lower Part of the Table)[a]

concentration/solvent	0.92 mM **6**/CH$_3$CN			2.40 mM **6**/CH$_3$CN		
electrochemical reactions	$E°$	α	k_s	$E°$	α	k_s
AcylCN + e ⇌ AcylCN$^{•-}$	−1.487	0.5	0.24	−1.486	0.5	0.14
Bz + e ⇌ Bz$^{•-}$	−1.555	0.5	0.03	−1.566	0.5	0.03
chemical reactions	K	k_f	k_b	K	k_f	k_b
2AcylCN$^{•-}$ ⇌ (AcylCN)$_2^{2-}$	1.0×10^8	1.2×10^4	1.2×10^{-4}	1.2×10^4	1.2×10^4	1.2×10^{-4}
(AcylCN)$_2^{2-}$ ⇌ BzCN$^-$ + CN	1.0×10^8	1.0×10^{10}	1.0×10^2	1.0×10^8	1.0×10^{10}	1.0×10^2
BzCN$^-$ ⇌ ManCN	1.0×10^8	2.8×10^8	2.8	1.0×10^8	2.8×10^8	2.8
BzCN$^-$ ⇌ Bz + CN	1.3×10^5	1.8×10^9	1.4×10^4	1.3×10^5	1.8×10^9	1.4×10^4
AcylCN$^{•-}$ + Bz ⇌ Bz$^{•-}$ + AcylCN	0.07	3.5×10^3	5.0×10^4	0.04	3.5×10^3	8.8×10^4
D of all species/cm^2/s		2.1×10^{-5}			2.1×10^{-5}	
concentration/solvent	1.30 mM **6**/DMF			3.75 mM **6**/DMF		
electrochemical reactions	$E°$	α	k_s	$E°$	α	k_s
AcylCN + e ⇌ AcylCN$^{•-}$	−1.451	0.5	0.10	−1.451	0.5	0.10
Bz + e ⇌ Bz$^{•-}$	−1.518	0.5	0.01	−1.518	0.5	0.01
chemical reactions	K	k_f	k_b	K	k_f	k_b
2AcylCN$^{•-}$ ⇌ (AcylCN)$_2^{2-}$	1.0×10^8	1.5×10^3	1.5×10^{-5}	1.0×10^8	1.1×10^3	1.1×10^{-5}
(AcylCN)$_2^{2-}$ ⇌ BzCN$^-$ + CN	1.0×10^8	1.0×10^{10}	1.0×10^2	1.0×10^8	1.0×10^{10}	1.0×10^2
BzCN$^-$ ⇌ ManCN$^-$	1.0×10^8	8.3×10^4	8.3×10^{-4}	1.0×10^8	8.3×10^4	8.3×10^{-4}
BzCN$^-$ ⇌ Bz + CN	30	1.0×10^6	3.3×10^4	30	1.0×10^6	3.3×10^4
D of all species/cm^2/s		5.7×10^{-6}			5.7×10^{-6}	

[a] The same values were used to fit all scan rates from 0.1 to 30 V/s. $E°$ potentials are in V and refer to the formal potential of the ferrocenium/ferrocene couple, k_s in cm/s, second-order rate constants in M^{-1} s^{-1}, first-order rate constants in s^{-1}. For acetonitrile, 120 Ω of solution resistance was electronically compensated, and the remaining 20 Ω was applied in the simulation. For DMF, 240 Ω was electronically compensated, and 40 Ω was applied in the simulation. AcylCN: benzoyl cyanide. AcylCN$^{•-}$: benzoyl cyanide anion radical. Bz: benzil. Bz$^{•-}$: benzil anion radical. Acyl(CN)$_2^{2-}$: benzil dicyanohydrin dianion. BzCN$^-$: anion of monocyanohydrin of benzil. ManCN$^-$: anion of mandelonitrile benzoate.

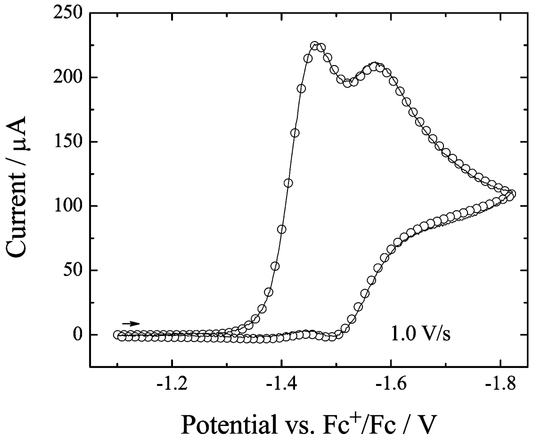

FIGURE 5. Voltammogram of 2.15 mM benzoyl cyanide, **6**, in acetonitrile containing 0.33 M water.

reacts by two parallel paths: reversible expulsion of cyanide to give the benzil, **5**, and rearrangement to the anion of the mandelonitrile benzoate, **4**. We find that some benzil is produced even in the absence of added water, a conclusion that is not evident from the preparative electrolyses.[14] Our observed enhancement of the rate of dimerization by added water helps to explain the outcome of electrosynthetic procedures.[14]

Results and Discussion

Figure 1 shows voltammograms for 2.40 mM benzoyl cyanide, **6**, in acetonitrile containing 0.10 M tetra-*n*-butylammonium hexafluorophosphate (Bu$_4$NPF$_6$). The scan rates were 0.20 (A), 2.00 (B), and 20.0 V/s (C). At the slowest scan rate (A), the principal reduction peak is irreversible and it is followed by a very small peak. The dotted curve in A is a voltammogram of 2.00 mM benzil. The agreement of the peak potential for benzil with that of the small second peak supports the conclusion that some benzil is being formed in these low scan rate experiments. At 2.00 V/s (B), the benzil reduction appears as a very small shoulder on the main peak and also there is some reversibility to the main peak. Finally, at 20.0 V/s (C), benzil is not detected and there is a large anodic peak associated with the main reduction peak.

A tentative assignment is that the main reduction peak is due to the reduction of benzoyl cyanide to its anion radical (reaction 1), which is followed by dimerization of the anion radical to produce dimeric dianion intermediate **2**. At larger scan rates, the dimerization reaction is incomplete so that a large anodic peak for oxidation of the anion radical (reverse of reaction 1) is detected. Given sufficient time, **2** reacts to form some benzil, **5**, via reactions 3 and 5, as seen in curves A and B. Direct detection of the anion of mandelonitrile benzoate, **4**, formed in reaction 4, is not possible as it is undoubtedly reduced at a potential more negative that mandelonitrile benzoate itself, −2.35 V versus ferrocene in *N*,*N*-dimethylformamide (DMF).[15]

Digital simulation of the voltammetric data was used to test the validity of the suggested mechanism (reactions 1−5). To see if the data are properly accounted for by a second-order dimerization of the anion radicals of **6**, data were obtained at two different concentrations, 0.92 and 2.40 mM. It was found that the same value of the dimerization rate constant, 1.2×10^5 M^{-1} s^{-1}, fits both sets of data. Examples of the fit of simulation to the data are shown in Figures 2 and 3. One can see that the simulations properly account for the relatively larger anodic peak

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(15) Zheng, Z.-R.; Lund, H. *J. Electroanal. Chem.* **1998**, *441*, 221−225.

TABLE 2. Experimental Conditions and Simulation Parameters for Benzoyl Cyanide, 6, in Acetonitrile Containing 0.33 M Water[a]

concentration/solvent	0.65 mM **6**/CH_3CN + 0.33 M H_2O			2.15 mM **6**/CH_3CN + 0.33 M H_2O		
electrochemical reactions	$E°$	α	k_s	$E°$	α	k_s
$\mathrm{AcylCN} + e \rightleftharpoons \mathrm{AcylCN}^{\bullet-}$	−1.451	0.5	0.10	−1.448	0.5	0.11
$\mathrm{Bz} + e \rightleftharpoons \mathrm{Bz}^{\bullet-}$	−1.524	0.5	0.05	−1.532	0.5	0.05
chemical reactions	K	k_f	k_b	K	k_f	k_b
$2\mathrm{AcylCN}^{\bullet-} \rightleftharpoons (\mathrm{AcylCN})_2^{2-}$	1.0×10^8	3.1×10^5	3.1×10^{-3}	1.0×10^8	3.1×10^5	3.1×10^{-3}
$(\mathrm{AcylCN})_2^{2-} \rightleftharpoons \mathrm{BzCN}^- + \mathrm{CN}$	1.0×10^8	1.0×10^{10}	1.0×10^2	1.0×10^8	1.0×10^{10}	1.0×10^2
$\mathrm{BzCN}^- \rightleftharpoons \mathrm{ManCN}^-$	1.0×10^8	4.6×10^7	4.6×10^{-1}	1.0×10^8	4.6×10^7	4.6×10^{-1}
$\mathrm{BzCN}^- \rightleftharpoons \mathrm{Bz} + \mathrm{CN}$	5.0×10^5	7.0×10^9	1.4×10^4	5.0×10^5	7.0×10^9	1.4×10^4
$\mathrm{AcylCN}^{\bullet-} + \mathrm{Bz} \rightleftharpoons \mathrm{Bz}^{\bullet-} + \mathrm{AcylCN}$	5.8×10^{-2}	1.3×10^7	2.2×10^8	3.7×10^{-2}	1.3×10^7	3.5×10^8
$\mathrm{Bz}^{\bullet-} \rightleftharpoons \mathrm{prod}$	2.5	4.7	1.9	2.5	3.8	1.5
D of all species/cm^2/s		1.3×10^{-5}			2.2×10^{-5}	

[a] The same values were used to fit all scan rates from 0.1 to 30 V/s. $E°$ potentials are in V and refer to the formal potential of the ferrocenium/ferrocene couple, k_s in cm/s, second-order rate constants in M^{-1} s^{-1}, first-order rate constants in s^{-1}. Solution resistance (120 Ω) was electronically compensated, and the remaining 20 Ω was applied in the simulation. AcylCN: benzoyl cyanide. $\mathrm{AcylCN}^{\bullet-}$: benzoyl cyanide anion radical. Bz: benzil. $\mathrm{Bz}^{\bullet-}$: benzil anion radical. $\mathrm{Acyl(CN)}_2^{2-}$: benzil dicyanohydrin dianion. BzCN^-: anion of monocyanohydrin of benzil. ManCN^-: anion of mandelonitrile benzoate anion.

TABLE 3. Experimental Conditions and Simulation Parameters for *p*-Methoxybenzoyl Cyanide, 7, in Acetonitrile (Upper Part of the Table) and Acetonitrile Containing 0.33 M Water (Lower Part of the Table)[a]

concentration/solvent	1.23 mM **7**/CH_3CN			2.50 mM **7**/CH_3CN		
electrochemical reactions	$E°$	α	k_s	$E°$	α	k_s
$\mathrm{AcylCN} + e \rightleftharpoons \mathrm{AcylCN}^{\bullet-}$	−1.610	0.5	0.15	−1.619	0.5	0.15
$\mathrm{Bz} + e \rightleftharpoons \mathrm{Bz}^{\bullet-}$	−1.687	0.5	0.07	−1.687	0.5	0.07
chemical reactions	K	k_f	k_b	K	k_f	k_b
$2\mathrm{AcylCN}^{\bullet-} \rightleftharpoons (\mathrm{AcylCN})_2^{2-}$	1.0×10^8	6.6×10^4	6.6×10^{-4}	1.0×10^8	6.6×10^4	6.6×10^{-4}
$(\mathrm{AcylCN})_2^{2-} \rightleftharpoons \mathrm{BzCN}^- + \mathrm{CN}$	1.0×10^8	1.0×10^{10}	1.0×10^2	1.0×10^8	1.0×10^{10}	1.0×10^2
$\mathrm{BzCN}^- \rightleftharpoons \mathrm{ManCN}^-$	1.0×10^8	4.8×10^3	4.8×10^{-5}	1.0×10^8	4.8×10^3	4.8×10^{-5}
$\mathrm{BzCN}^- \rightleftharpoons \mathrm{Bz} + \mathrm{CN}$	1.0×10^8	1.2×10^4	1.2×10^{-4}	1.0×10^8	1.3×10^4	1.3×10^{-4}
$\mathrm{AcylCN}^{\bullet-} + \mathrm{Bz} \rightleftharpoons \mathrm{Bz}^{\bullet-} + \mathrm{AcylCN}$	4.9×10^{-2}	1.0×10^8	2.1×10^9	7.1×10^{-2}	1.0×10^8	1.4×10^9
D of all species/cm^2/s		2.3×10^{-5}			2.0×10^{-5}	
concentration/solvent	1.82 mM **7**/CH_3CN + 0.33 M H_2O			3.70 mM **7**/CH_3CN + 0.33 M H_2O		
electrochemical reactions	$E°$	α	k_s	$E°$	α	k_s
$\mathrm{AcylCN} + e \rightleftharpoons \mathrm{AcylCN}^{\bullet-}$	−1.586	0.5	0.23	−1.580	0.5	0.23
$\mathrm{Bz} + e \rightleftharpoons \mathrm{Bz}^{\bullet-}$	−1.675	0.5	0.12	−1.671	0.5	0.12
chemical reactions	K	k_f	k_b	K	k_f	k_b
$2\mathrm{AcylCN}^{\bullet-} \rightleftharpoons (\mathrm{AcylCN})_2^{2-}$	1.0×10^8	1.8×10^5	1.8×10^{-3}	1.0×10^8	1.8×10^5	1.8×10^{-3}
$(\mathrm{AcylCN})_2^{2-} \rightleftharpoons \mathrm{BzCN}^- + \mathrm{CN}$	1.0×10^8	1.0×10^{10}	1.0×10^2	1.0×10^8	1.0×10^{10}	1.0×10^2
$\mathrm{BzCN}^- \rightleftharpoons \mathrm{ManCN}^-$	1.0×10^8	2.3×10^3	2.3×10^{-5}	1.0×10^8	2.3×10^3	2.3×10^{-5}
$\mathrm{BzCN}^- \rightleftharpoons \mathrm{Bz} + \mathrm{CN}$	1.0×10^8	1.0×10^4	1.0×10^{-4}	1.0×10^8	1.0×10^4	1.0×10^{-4}
$\mathrm{AcylCN}^{\bullet-} + \mathrm{Bz} \rightleftharpoons \mathrm{Bz}^{\bullet-} + \mathrm{AcylCN}$	3.1×10^{-2}	1.0×10^8	3.2×10^9	2.8×10^{-2}	1.0×10^8	3.6×10^9
$\mathrm{Bz}^{\bullet-} \rightleftharpoons \mathrm{prod}$	1.0×10^8	0.5	5.0×10^{-9}	1.0×10^8	0.5	5.0×10^{-9}
D of all species/cm^2/s		2.0×10^{-5}			2.2×10^{-5}	

[a] Other conditions as in Table 2.

seen for the lower concentration (Figure 2), which in turn is related to the fact that the relative rate of a second-order reaction decreases with decreases in concentration.

Also included in the simulations was reaction 3 followed by parallel reactions 4 and 5, which afford the two products reported in the electrosynthetic work, **4** and **5**.[14] We also included the one-electron reduction of benzil to its anion radical. The effect of these reactions is difficult to see in Figures 2 and 3 because there is no apparent shoulder for the reduction of benzil. However, at low scan rates there is a small peak or shoulder that must be reproduced by the simulation. An example is shown in Figure 4. It should be emphasized that the same set of simulation parameter values was found to fit all of the scan rates, from 0.10 to 30 V/s. Thus, the quality of the fit for any given scan rate, say Figure 4, might be improved by adjustment of parameter values, but such adjustment would lead to poorer fits at other scan rates.

The simulation parameter values used for **6** in acetonitrile are listed in Table 1. Reactions 2−4 were treated as totally irreversible reactions (large equilibrium constant). However, the equilibrium constant for reaction 5 could not be made as large (i.e., some reversibility was needed).[15] Reaction 3, which forms the anion of the monocyanohydrin of benzil, was treated as being extremely fast with the rate constants for reactions 4 and 5 being adjusted to achieve good fits. The inclusion of the homogeneous exchange reaction between the anion radical of benzoyl cyanide and benzil was found to improve the quality of the fits. Other examples of the fits of simulations to the voltammograms of **6** in acetonitrile are included in the Supporting Information (Figures S1 and S2).

TABLE 4. Experimental Conditions and Simulation Parameters for *p*-Chlorobenzoyl Cyanide, 8, in Acetonitrile Containing 0.33 and 0.66 M Water[a]

concentration/solvent	2.20 mM **8**/CH_3CN + 0.33 M H_2O			2.19 mM **8**/CH_3CN + 0.66 M H_2O		
electrochemical reactions	$E°$	α	k_s	$E°$	α	k_s
AcylCN + e ⇌ $AcylCN^{\bullet -}$	−1.368	0.5	0.09	−1.348	0.5	0.09
Bz + e ⇌ $Bz^{\bullet -}$	−1.401	0.5	0.08	−1.395	0.5	0.08
chemical reactions	K	k_f	k_b	K	k_f	k_b
2$AcylCN^{\bullet -}$ ⇌ $(AcylCN)_2^{2-}$	1.0×10^8	5.7×10^5	5.7×10^{-3}	1.0×10^8	8.0×10^5	8.0×10^{-3}
$(AcylCN)_2^{2-}$ ⇌ $BzCN^-$ + CN	1.0×10^8	1.0×10^{10}	100	1.0×10^8	1.0×10^{10}	100
$BzCN^-$ ⇌ $ManCN^-$	1.0×10^8	2.0×10^8	2.0	1.0×10^8	2.5×10^8	2.5
$BzCN^-$ ⇌ Bz + CN	9.0×10^4	3.0×10^9	3.3×10^4	2.0×10^5	3.0 × 109	1.5×10^4
$AcylCN^{\bullet -}$ + Bz ⇌ $Bz^{\bullet -}$ + AcylCN	0.27	1.0×10^8	3.7×10^8	0.16	1.0×10^8	6.3×10^8
D of all species/cm^2/s		1.4×10^{-5}			1.3×10^{-5}	

[a] Other conditions as in Table 2.

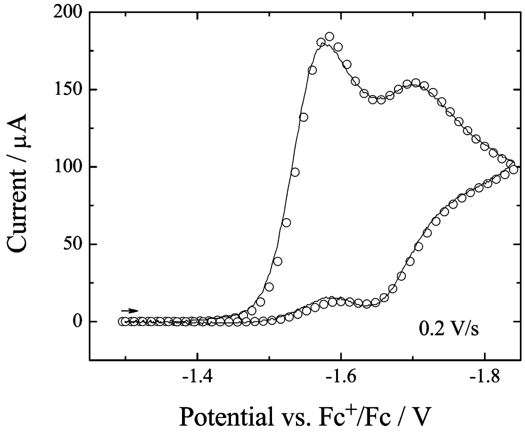

FIGURE 6. Voltammogram of 3.70 mM *p*-methoxybenzoyl cyanide, **7**, in acetonitrile with 0.33 M water.

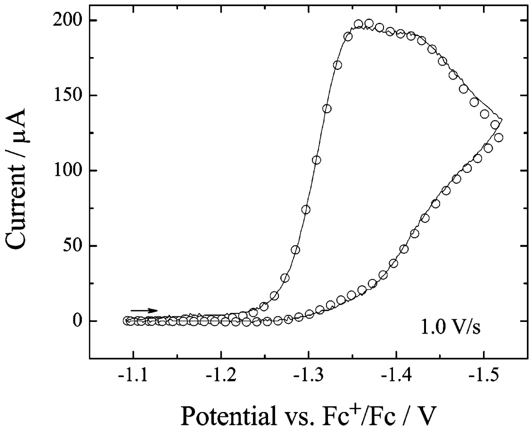

FIGURE 7. Voltammogram of 2.19 mM *p*-chlorobenzoyl cyanide, **8**, in acetonitrile with 0.66 M water.

Data were also obtained for two concentrations of **6** in DMF, and the best-fit simulation parameter values are also included in Table 1. The most notable feature is that the average dimerization rate constant, 1.3×10^3 M^{-1} s^{-1}, is an order of magnitude smaller than that observed in acetonitrile. The same trend has been observed in the dimerization of anion radicals of aromatic aldehydes.[16] Thus, at any given scan rate, less dimer is formed and consequently less benzil is detected in the voltammetry. Examples of fits of voltammograms of **6** in DMF are included in the Supporting Information (Figures S3 and S4).

In the electrosynthetic work,[14] it was demonstrated that the formation of benzil is enhanced by adding water. An example of a voltammogram of **6** in acetonitrile containing 0.33 M water is shown in Figure 5, where the benzil peak is much more pronounced than in the absence of added water. Fits of simulations to the voltammograms were successful over the range of 0.1−30 V/s, and the simulation parameters are shown in Table 2. In this case, the addition of water causes an increase in the rate constant for dimerization of the anion radicals by about a factor of 25.

A similar effect of water was seen with aromatic aldehydes,[16] where it was shown that enhanced dimerization rates correlated with the hydrogen bond donating capability of the additive, water in the present case. To achieve adequate fits, it was necessary to include slow loss of the anion radical of benzil, an observation that was confirmed by studies of benzil itself. Other examples of fits of simulations to the voltammograms of **6** in acetonitrile with 0.33 M water are given in the Supporting Information (Figures S5 and S6).

It was found that even more benzil is formed on the voltammetric time scale when **6** is studied in acetonitrile/water (85% acetonitrile, v/v). In the electrosynthetic work,[14] this mixed solvent also produced the highest yields of benzil. Due to the complexity of the voltammetric response, we did not attempt to fit the voltammograms.

Also investigated were *p*-methoxybenzoyl cyanide, **7**, and *p*-chlorobenzoyl cyanide, **8**. When studied in acetonitrile in the absence of added water, the behavior of **7** was similar to that of **6** though the peak assigned to the reduction of 4,4′-dimethoxybenzil was somewhat more pronounced. The dimerization rate constant, 6.6×10^4 M^{-1} s^{-1}, was about five times larger than that seen for **6**. As expected, both the standard potentials for reduction of **6** and for reduction of the corresponding benzil are shifted ca. 0.13 V in the negative direction due to the electron-donating properties of the methoxy substituent. Simulation parameters are given in Table 3, and examples of fits of simulations to the voltammograms of **7** in acetonitrile are presented in the Supporting Information (Figures S7 and S8)

As with **6**, the reduction of **7** is affected by added water. Figure 6 shows a voltammogram of 3.70 mM **7** with 0.33 M water, which reveals a pronounced peak for reduction of the corresponding benzil. In this case, water again has the effect of increasing the dimerization rate constant but only by about a factor of 3 compared to that of **6**. The standard potentials are

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(16) Van Kirk, C. C.; Fioravanti, G.; Mattiello, L.; Rampazzo, L. B.; Macías-Ruvalcaba, N. A.; Evans, D. H. *J. Electroanal. Chem.* **2005**, *582*, 151−155.

more negative than those of **6** by about 0.14 V. Simulation parameters are also given in Table 3, and other examples of fits of simulations to the voltammograms of **7** in acetonitrile with 0.33 M water are given in the Supporting Information (Figures S9 and S10).

We were not able to fit the voltammograms of chloro derivative **8** for acetonitrile with no added water. The principal difficulty is that the peak for reduction of 4,4′-dichlorobenzil is not well resolved from the main reduction peak. Somewhat clearer results were obtained in the presence of water. Figure 7 shows data for 2.19 mM **8** in acetonitrile with 0.66 M water at 1.00 V/s. Data with 0.33 M added water were also fit by simulation; the simulation parameters for both water concentrations are given in Table 4, and other examples of fits of simulations to the voltammograms of **8** in acetonitrile with 0.33 and 0.66 M water are given in the Supporting Information (Figures S11 and S12).

At 0.33 M water, where comparison among the three compounds is possible, the dimerization rate constant decreases in the order X = Cl (**8**) (5.7×10^5 M^{-1} s^{-1}) > X = H (**6**) (3.1×10^5 M^{-1} s^{-1}) > X = CH_3O (**7**) (1.8×10^5 M^{-1} s^{-1}). This small effect may be due to the ability of the electron-withdrawing substituent to lower the energy of the transition state where the two negatively charged acyl anions, $ArC(O)^-$, come together to dimerize. Interestingly, in the absence of added water the trend is reversed for **6** and **7** (see Tables 1 and 3). In the case of the chloro derivative with 0.33 M water, the standard potentials for reduction of **8** and its corresponding benzil are shifted in the positive direction by 0.08 and 0.12 V, respectively, compared to those of **6**. These shifts, of course, are caused by the electron-withdrawing nature of the chloro substituent. Also, for **6** and **7** the standard potentials for the benzoyl cyanide/benzoyl cyanide anion radical couple and for the benzil/benzil anion radical couple are shifted slightly (12−40 mV) toward less negative potentials in acetonitrile with 0.33 M water compared to that with no added water. These shifts reflect hydrogen-bonding interactions of water with the anion radicals.

All three compounds, **6**−**8**, were studied in the electrosynthetic work, and the yields of benzil obtained in acetonitrile/water were very similar, 62−67%.[14]

Conclusion

The electrochemical reduction of three benzoyl cyanides has been shown to occur by reactions 1−5 in acetonitrile both with and without added water. The same mechanism was found to hold for benzoyl cyanide in DMF. The mechanism consists of the initial formation of anion radicals that undergo a relatively rapid dimerization reaction. The resulting dimer dianion, **2**, loses cyanide to produce the anion of the monocyanohydrin of benzil, **3**. This final species participates in two parallel reactions: loss of cyanide to form benzil, **5**, and rearrangement to the anion of mandelonitrile benzoate, **4**. We have found that small amounts of benzil are formed in the absence of added water, and, consistent with the electrosynthetic results,[14] benzil formation is enhanced in the presence of water.

Experimental Section

Chemicals and Reagents. The solvent for electrochemistry was acetonitrile or *N*,*N*-dimethylformamide, and the electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate. Sources and treatment of the solvents and electrolyte have been described.[17] Benzoyl cyanide, **6**, was a commercial sample. Benzoyl cyanides **7** and **8** were prepared by reaction of 0.02 mol of the corresponding benzoyl chloride with 0.023 mol of cuprous cyanide according to the methodology described by Oakwood and Weisgerber[18] and were purified by column chromatography with 90:10 hexane/ethyl acetate mixture as eluent, followed by recrystallization from hexane (**7**, mp 58.7−59.9 °C, lit. 56.5−57.5 °C,[19] lit. 59.0 °C;[20] **8**, mp 41.5−42.3 °C, lit. 41−42 °C,[19] lit. 42.0 °C[20]).

Electrochemical Cells, Electrodes, and Instrumentation. These were as described earlier.[17] The working electrode was a 0.3-cm-diameter glassy carbon electrode whose area was determined to be 0.0814 cm^2. The reference electrode was a silver wire immersed in 0.10 M Bu_4NPF_6/0.010 M $AgNO_3$ in acetonitrile. The potential of this reference electrode was periodically measured versus the reversible ferrocene/ferrocenium potential, and all potentials reported in this work are with respect to ferrocene. Evaluation of the solution resistance has been described.[17] The temperature was maintained at 298 K.

Variation of the scan rate, v, was done in such a way that there was an approximately linear variation in log v. Thus, for scan rates between 0.1 and 30 V/s, the values chosen were 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 5, 10, 20, and 30 V/s (log $v = -1, -0.699, -0.523, -0.301, 0, 0.301, 0.477, 0.699, 1, 1.301, 1.477$).

Digital simulations were conducted with the aid of DigiElch, version 2.0, a free software package for the **Digi**tal simulation of common **El**ectro**ch**emical experiments (http://www.digielch.de).[21] Part of the solution resistance was compensated electronically, and the remainder was included in the simulation program.

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Supporting Information Available: Examples of fits of simulation to background-corrected voltammograms of **6**−**8** under various conditions (Figures S1−S12). This material is available free of charge via the Internet at http://pubs.acs.org.

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