The electrochemical reduction of benzil, as a representative aromatic α-diketone, has been widely studied in both protic and nonaqueous solvents. In nonaqueous solvents, the reduction generally occurs in two successive one-electron steps, the first of which is relatively uncomplicated. The second step, which produces the stilbenediol cation, is considerably more involved due to the protonation of the dianion by the solvent, leading to mostly irreversible behavior for the second step. In addition, the possibility of cis and trans isomers for the one- and two-electron reduction products gives rise to a sometimes bewildering array of benzil reduction pathways. In the present work, the behavior of benzil is reported in the ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (BDMIm BF₄), and 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate (BMPY TfO). The ability of the ionic liquids to interact with the benzil reduction products is clearly evident from the results, principally due to the proton donating abilities of some of the cationic ring systems. Finally, the effect of various Lewis acid additions on benzil electrochemistry has also been investigated. A similar study of 9-fluorenone in various ionic liquids has been previously published.

**Experimental**

Cyclic voltammograms were obtained using a PAR 283 potentiostat and PowerSuite software, and potentials are reported with respect to a Ag/AgCl (0.10 M EMIm Cl / EMIm BF₄) reference electrode (Cypress Systems). Glassy carbon electrodes (GC, 1 mm diameter) were obtained from Cypress Systems or EDAX Inc. All electrochemical experiments were carried out in a Vacuum Atmospheres glove box at ambient temperature (~22 °C). All chemicals were of analytical grade. EMIm Cl and NaBF₄ were purchased from EM Science. EMIm BF₄ was prepared by metathesis of MEIm Cl and NaBF₄. Acetonitrile was purified by distillation in a closed tube over aluminum wire. Tetraethylammonium tetrafluoroborate (TEA BF₄) was purchased from Sachem (formerly Southwestern Analytical Chemicals). AlCl₃ was obtained from Fluka and was purified by distillation in a closed tube over aluminum wire. Tetraethylammonium tetrafluoroborate (TEA BF₄, Electrometric grade) was purchased from Sachem (formerly Southwestern Analytical Chemicals). EMIm BF₄ was prepared by metathesis of EMIm Cl and NaBF₄. 1-Butyl-2,3-dimethylimidazolium tetrafluoroborate (BDMIm BF₄) was prepared by metathesis of BDMIm Cl and NaBF₄. All ionic liquids were dried on a high-vacuum line at 70 °C to 80 °C for 2–3 days before use. Benzil, acetonitrile (AN, anhydrous grade), and BF₄ ethereal (purified, redistilled grade) were obtained from Aldrich Chemical Company. AlCl₃ was obtained from Fluka and was purified by distillation in a closed tube over aluminum wire.

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addition of alkaline earth salts to acetonitrile/benzil solutions\textsuperscript{14} and as reported for 9-fluorenone in this system.\textsuperscript{29} As was the case for benzil in acetonitrile above, the scan rate dependence of the benzil voltammetry in EMIm BF\textsubscript{4} suggests the involvement of a slow step in the reduction pathway, the most likely nature of which is a proton abstraction from the EMIm cation.\textsuperscript{28,29} The reaction scheme given in Figure 3 is consistent with the voltammetry shown in Figure 2. At low scan rates (100 mV/s), there is time for the one-electron reduction product to be protonated, and the subsequent rearrangement to the benzoin radical species sets the stage for its one-electron reduction, protonation, and following two-electron reduction. Considering that these last reduction processes take place at similar potentials, this scheme accounts for the much larger current response at \(-1.7\) V compared to that at \(-0.8\) V. Increasing the scan rate and thus eliminating the first protonation allows only the second reduction process to occur, giving roughly equal currents for the two processes. Note that the second reduction process is not reversible, probably due to protonation of the benzil dianion by the EMIm ring. For further confirmation of the proposed reduction pathway, additions of EMIm BF\textsubscript{4} (via microsyringe) were made to a solution of benzil in acetonitrile. After an addition of 3:1 EMIm BF\textsubscript{4}:benzil, the cyclic voltammogram closely resembled that of benzil in EMIm BF\textsubscript{4}, consistent with the role of the EMIm cation as proton donor for the benzil reduction products.

In support of the proposed mechanism, the voltammetry of benzil in BDMIm BF\textsubscript{4}, which does not have an acidic proton in the 2 position, has been briefly studied.\textsuperscript{25} Figure 4 shows that the first reduction process is reversible at 100 mV/s, whereas in EMIm BF\textsubscript{4} the effect of proton donation to the radical anion greatly distorted this process at 100 mV/s. The remaining two reduction processes in Figure 4 have not been fully explored; however, they have counterparts in the voltammogram of benzil in EMIm BF\textsubscript{4} at 1000 mV/s (Figure 2).

As in a previously reported study of 9-fluorenone,\textsuperscript{29} the complexation of benzil by BF\textsubscript{3} was studied by adding BF\textsubscript{3} etherate to a solution of benzil in EMIm BF\textsubscript{4}. As shown in Figure 5, a new reduction peak, evidently corresponding to a benzil:BF\textsubscript{3} complex, appears at \(-0.3\) V as BF\textsubscript{3} etherate is added. The complexation is virtually complete upon equimolar addition of BF\textsubscript{3} etherate to benzil. By contrast, 9-fluorenone and benzophenone are not fully complexed until more than twice the molar amount of BF\textsubscript{3} etherate has been added.\textsuperscript{25,29} This finding indicates that benzil forms a more stable complex with BF\textsubscript{3} than do 9-fluorenone and benzophenone, probably due to the involvement of both benzil carbonyl groups in the complexation.

**Electrochemistry of benzil in BMPY TfO.**—The electrochemical behavior of benzil in BMPY TIO presents an interesting contrast to its behavior in EMIm BF\textsubscript{4}. As can be observed from Figure 6a, benzil undergoes electrochemical reduction in BMPY TIO in two successive, reversible electron-transfer steps which form the radical anion and then the dianion. Similar behavior is observed for 9-fluorenone in BMPY TIO,\textsuperscript{29} indicating that the radical anions and dianions for each system are stable in this ionic liquid. In contrast, reduction of benzil in other nonaqueous solvents such as acetonitrile (Figure 1), N,N-dimethylformamide,\textsuperscript{14,16} and EMIm BF\textsubscript{4} (Figure 2) involves considerable irreversibility for the second process. In these cases, the solvents possess activated hydrogen atoms which act as proton donors for the dianions, resulting in protonated species which are no longer oxidizable at the original potentials. The BMPY cation, however, has an aliphatic quaternary ammonium ring system and no activated hydrogen atoms in the system. The low proton donating ability of BMPY TIO, then, accounts for the reversible behavior seen for benzil and 9-fluorenone in BMPY TIO. The ionic liquid BMPY TIO serves as a suitable solvent for observing relatively uncomplicated voltammetric behavior of benzil and probably other similar systems. These results also present the possibility of studying the effect of added proton donors in this solvent.
The effectiveness of acetonitrile as a proton donor toward benzil reduction products can be seen in Figure 7, in which increasing amounts of acetonitrile have been added to benzil in BMPY TFO. It is obvious from Figure 7 that a relatively large amount of acetonitrile is necessary to cause voltammetric changes due to proton donation from acetonitrile. The rather large increases in current are due to the dramatic decrease in the viscosity of the ionic liquid upon addition of acetonitrile, which may also affect the availability of acetonitrile as a proton donor. Eventually, the additions of acetonitrile are sufficient to cause the voltammetry to be essentially the same as that in acetonitrile/TEA BF₄ as seen in Figure 1. It should be noted that reversal of the potential scan past the first reduction process gives a reversible response in all cases, signifying that the radical anion formed in the first reduction process is not protonated by the added acetonitrile. The mechanistic pathway at this point is evidently the same in BMPY TFO/AN as it is in AN/TEA BF₄. An approximate lower value of the pKₐ value for the protonated dianion can be found from the calculated pKₐ = 31.3 for acetonitrile in DMSO. A rather high concentration of acetonitrile is required to observe protonation effects, so the pKₐ for the protonated dianion is probably also approximately 31 in the BMPY TFO/AN system. As referenced to water (vs in DMSO), acetonitrile has a pKₐ = 25 suggesting a similar value for the protonated dianion on the water reference scale.

**Conclusions**

The electrochemical characteristics of benzil have been investigated in the ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIm BF₄) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (BDMIm BF₄). From previous studies, it has been found that the EMIm cation can interact with reduction products of these ketones by complex formation, and the present study has shown that the EMIm...
cation can also protonate some of these reduction products. Although the fluorenone radical anion is not protonated by EMIm cation,29 the radical anions of both benzophenone25 and benzil undergo extensive protonation at 100 mV/s. The protonation process is rather slow, however, and the effects can be largely avoided at 1000 mV/s. In the BDMIm BF₄ ionic liquid, the acidic 2 position of the imidazolium ring is blocked by a methyl group, and protonation of the radical anions is not observed. In contrast to investigations in commonly employed nonaqueous solvents, benzil undergoes two successive reversible one-electron redox processes in the room-temperature ionic liquid BMPY TfO. This behavior is due to the lack of proton donation from the BMPY cation to the reduced species formed in the reduction process. In the BMPY TFO solvent system, the only possible proton source is the BMPY cation, which is actually a quaternary ammonium cation and therefore has very limited proton donation ability. Addition of acetonitrile to a solution of benzil in BMPY TFO caused the second reduction process, which involves the formation of the benzil dianion, to become irreversible due to its protonation by acetonitrile.

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