Observation by Cyclic Voltammetry of the Addition of Electrogenerated $^{-}CH_2CN$ to Aromatic Carbonyl Compounds

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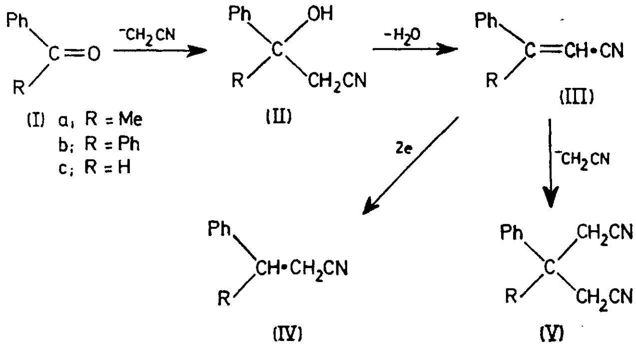
Summary The rapid addition of $^{-}CH_2CN$ to the carbonyl group of acetophenone and benzophenone has been detected by cyclic voltammetry using mixtures of the ketones and azobenzene in acetonitrile, the azobenzene being added to generate $^{-}CH_2CN$ in the vicinity of the electrode.

We recently reported[1] that the electro-reduction of aromatic carbonyl compounds (I) in dry acetonitrile gave significant amounts of 3-substituted propiononitriles (IV) and glutaronitriles (V). By analogy with the known reaction of the conjugate base of acetonitrile with carbonyl compounds[2] we suggested that the first step in the formation of these products involves the addition of $^{-}CH_2CN$, generated initially by reduction to give pinacol and subsequently by reduction of an $\alpha\beta$-unsaturated nitrile (III) to give the propiononitrile and hydrodimer, to the carbonyl group to form a hydroxynitrile (II).



We now present evidence from cyclic voltammetry studies which supports this suggestion and which indicates that the addition is fast. The reduction of azobenzene in acetonitrile is reported[3] to involve two one-electron transfer steps followed by rapid protonation of the dianion, thus generating $^-CH_2CN$. Since both electron-transfer steps for azobenzene occur less cathodic than the first electron transfer of acetophenone (Ia), azobenzene can be used electroanalytically to generate $^-CH_2CN$ in the vicinity of the electrode,[4] and the amount of addition of $^-CH_2CN$ to acetophenone occurring during the time-scale of the cyclic voltammetry experiment (sweep rate: 230 mV/s) can be monitored by the decrease in $i_{p,c}$ for the first electron-transfer of acetophenone. We have observed that the addition of increasing amounts of azobenzene to the acetophenone solution causes a progressive decrease in $i_{p,c}$ for acetophenone, *e.g.* for a solution 2 mM in both components, $i_{p,c}$ is only 45% of the $i_{p,c}$ in the absence of azobenzene (Figure). The addition of azobenzene also causes the first electron-transfer step of acetophenone to become more reversible (Figure; $i_{p,a}/i_{p,c}$ 0·38 → 0·85). This is probably caused by traces of proton donors being scavenged by the azobenzene dianion.

Similar results were obtained with benzophenone (Ib). However, in this case the second and first reduction peaks of azobenzene and benzophenone respectively coincide and the portion of the composite peak due to benzophenone can only be calculated by assuming that $i_{p,c}$ (**2**)/$i_{p,c}$ (**1**) for azobenzene remains unchanged in the presence of benzophenone.† In this case a solution 2mM in both components gives an $i_{p,c}$ for benzophenone only 30% of the $i_{p,c}$ in the absence of azobenzene.

Control experiments performed in $HCONMe_2$ using 2,2′-azonaphthalene[5] instead of azobenzene‡ showed there was no decrease in $i_{p,c}$ for benzophenone on addition of an equimolar amount of the azo-compound, but there was a 40% decrease in $i_{p,c}$ for acetophenone. The latter is probably caused by proton abstraction from the acetyl group and suggests that this mode of reaction may contribute to the decrease observed for acetophenone in acetonitrile. However, the absence of any decrease in $i_{p,c}$ for benzophenone in $HCONMe_2$ indicates that nucleophilic addition of the dianion of the azo-compound[6] to the carbonyl group is not responsible for the decreases observed for both ketones in acetonitrile. For benzophenone, the decrease in $i_{p,c}$ in acetonitrile can be attributed entirely to the addition of $^-CH_2CN$ to the carbonyl group, whereas for acetophenone the decrease is probably caused by both addition and deprotonation.

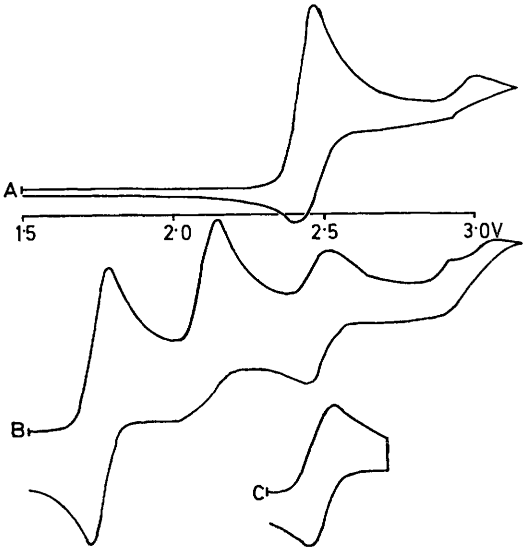


FIGURE. (A), 2 mM acetophenone; (B) and (C), 2 mM acetophenone + 2 mM azobenzene. MeCN solvent; 0·1 M Et_4NBF_4 electrolyte; stationary mercury electrode, reference Ag–$AgNO_3$ (0·1 M); 230 mV/s sweep rate.

The conversion of the $\alpha\beta$-unsaturated nitrile (III) into the glutaronitrile (V) involving Michael addition of $^-CH_2CN$ should be amenable to a similar study and is under investigation.

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† $i_{p,c}$ (**2**)/$i_{p,c}$ (**1**) for azobenzene remains unchanged in the presence of acetophenone.

‡ The electrochemical behaviour of the two azo-compounds is very similar in both $HCONMe_2$[5] and MeCN. 2,2′-Azonaphthalene had to be used in $HCONMe_2$ because the $E_{p,c}$ (**2**) of azobenzene is too cathodic; for these experiments $E_{p,c}$ (**2**) of the azo-compound must be equal to or preferably less than the $E_{p,c}$ (**1**) of the carbonyl compound. Unfortunately, 2,2′-azonaphthalene has a low solubility in MeCN and therefore the same azo-compound cannot be used for both solvents.

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