Cyclic Voltammetry of Azopyridines, Phenylazopyridines, and Azobenzene in Acetonitrile and Dimethylformamide

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The cyclic voltammetric behaviour of 2,2'-, 3,3'-, and 4,4'-azopyridine, and 2-, 3-, and 4-phenylazopyridine in CH_3CN is compared with that of azobenzene. From the results obtained when CH_3CN and $PhCH_2CO_2Et$ are added to solutions of azobenzene and 2,2'-azopyridine in super-dry dimethylformamide it is concluded that the azopyridines and phenylazopyridines are reduced by a mechanism analogous to that of azobenzene, and that their dianions deprotonate CH_3CN to give $^-CH_2CN$.

The electrochemical reduction of azobenzene [1-7] and substituted azobenzenes [2,3,6] has been extensively studied in both dimethylformamide (DMF) [1,2,4,6] and CH_3CN.[3,5,7] In CH_3CN, the dianion of azobenzene is reported [3b] to be protonated rapidly by the solvent generating the conjugate bases of hydrazobenzene and acetonitrile, and it was this observation which led us to use azobenzene in CH_3CN for the electrogeneration of $^-CH_2CN$, in an electroanalytical study of the addition of $^-CH_2CN$ to aromatic carbonyl compounds and α,β-unsaturated nitriles.[5,7] An important limitation to the use of azobenzene for this purpose, however, is the relatively high negative potential required for generation of the dianion [$E_{p,c}$ (2) −2.18 V *vs.* Ag–0.1M-$AgNO_3$–CH_3CN], restricting its use to the study of those carbonyl and α,β-unsaturated nitrile systems which have $E_{p,c}$ (1) −2.18 V, and preferably < −2.5 V [PhCOPh has $E_{p,c}$ (1) −2.19 V,[7] $PhCOCH_3$ has $E_{p,c}$ (1) −2.45 V,[7] PhCH=CHCN has $E_{p,c}$ (1) −2.19 V,[8] and CH_2=CHCN has $E_{p,c}$ (1) −2.52 V [8]].

In order to overcome this limitation we have investigated the use of other, more easily reduced azo-compounds as sources of $^-CH_2CN$. The reported $E_{\frac{1}{2}}/E_{p,c}$ (2) values for 2,2'- and 3,3'-azopyridine [$E_{\frac{1}{2}}$ (2) −1.65 and −1.85 V *vs.* Ag–AgCl–saturated KCl, respectively],[9] and 4,4'-azopyridine [$E_{\frac{1}{2}}$ (2) −1.53 V, $E_{p,c}$ (2) −1.55 V *vs.* saturated calomel electrode],[2] and the $E_{\frac{1}{2}}$ (1) value for 3-phenylazopyridine (−1.26 V *vs.* saturated calomel electrode),[10] all in DMF, suggested that a study of the isomeric azopyridines and phenylazopyridines might be rewarding. However we noted that, in contrast to azobenzene, the second electron transfer of 4,4'-azopyridine is not irreversible, $i_{p,a}/i_{p,c}$ being *ca.* 0.7 at *v* 300 mV s^{-1}.[2] Thus the dianion of 4,4'-azopyridine is less rapidly protonated (in Bu_4NClO_4–DMF) than the dianion of azobenzene. Similar behaviour is reported [3] for 4-nitroazobenzene in CH_3CN [$E_{\frac{1}{2}}$ (2) −1.195 V *vs.* saturated calomel electrode]. Not unexpectedly, therefore, there are conflicting requirements in this type of precursor for $^-CH_2CN$ between ease of reduction and fast deprotonation of CH_3CN by the dianion; those azo-compounds which are more easily reduced tend to give relatively stable dianions, and *vice versa*. Nevertheless, we report here the cyclic voltammetric behaviour of 2,2'-, 3,3'-, and 4,4'-azopyridine, and 2-, 3-, and 4-phenylazopyridine in CH_3CN.

Results and Discussion

The cyclic voltammetric data for these two series of compounds, in CH_3CN purified and dried by standard procedures,[11] are given in the Table. All the compounds, except perhaps 3,3'-azopyridine, show a reversible first electron transfer, with 4-phenylazopyridine the most easily reduced phenylazopyridine and 4,4'-azopyridine by far the most easily reduced azo-compound studied. The second electron transfer occurs at 0.40—0.62 V cathodic of the first electron transfer although the separation of the peak potentials for the first and second electron transfers ($\Delta E_{p,c}$) is probably dependent upon the concentration of proton donors other than CH_3CN itself (see below for specific cases).[12] In every case the oxidation peak corresponding to the second electron transfer is broad and smaller than the cathodic peak, but $i_{p,a}/i_{p,c}$ and $i_{p,c}$ (2)/$i_{p,c}$ (1) depend upon the concentration of proton donors present. The values for these functions given in the Table are for 'normal' conditions; the results for more anhydrous–aprotic conditions are described later. None of these azo-compounds exhibits an irreversible second electron transfer (*cf.* azobenzene), but on account of their ease of reduction [$E_{p,c}$ (2)], 2,2'- and 4,4'-azopyridine and 4-phenylazopyridine were selected for further study.

An estimate of the rate constant (*k*) for the chemical reaction following the second electron transfer to these systems under 'normal' conditions was obtained both by comparison with computer-simulated cyclic voltammograms, and by using the working curve for $i_{p,a}/i_{p,c}$ *vs.* log *k*τ.[13] All three compounds gave values within the range 0.5—4.0 s^{-1}, rather too low for their use as precursors of $^-CH_2CN$ in our electroanalytical test for reactivity towards $^-CH_2CN$; rate constants in excess of 10 s^{-1} are preferred, since below this value the measured reactivity towards $^-CH_2CN$ is no longer independent of the rate constant for generation of $^-CH_2CN$.[7]

When this work was in progress it was reported [6] that the cyclic voltammogram of azobenzene in DMF which had been dried by passing through a column of active neutral alumina (a technique pioneered by Parker and his co-workers [12]) showed two reversible electron-transfer processes, and that the cyclic voltammogram was not affected by the addition of acetonitrile (pK_a 25),[14] although addition of acetone (pK_a 20) [14] or t-butyl acetate (CH_3CO_2Et has pK_a 24.5) [14] caused the second electron transfer to become irreversible, presumably by protonation (see also ref. 4). These results cast some doubt upon the original proposal [3] that the irreversible nature of the second electron transfer to azobenzene in CH_3CN is due to proton abstraction from CH_3CN by the dianion, although the solvent and the concentration of the protonating agent in these two studies differ (*viz.* 10 mM *vs.* 1.9 × 10^4 mM for an azobenzene concentration of *ca.* 1 mM). Since the question of deprotonation of CH_3CN by the dianion of azobenzene is crucial to use of the latter as a precursor for $^-CH_2CN$, we examined azobenzene as well as 2,2'- and 4,4'-azopyridine under more strictly anhydrous–aprotic conditions in both CH_3CN and DMF; benzophenone and perylene were also included as they and azobenzene had been studied previously.[6,12]

In DMF containing 0.1M-Et_4NBF_4, the second electron transfer of azobenzene, 2,2'-azopyridine, and benzophenone became chemically reversible when neutral activated alumina was added to the solution and the suspension was cooled,

Table. Cyclic voltammetric data

Compound	$E_{p,c}$ (1) [a]	$E_{p,a}$ (1) [a]	$\frac{i_{p,a}}{i_{p,c}}$	$E_{p,c}$ (2) [a]	$E_{p,a}$ (2) [a]	$\frac{i_{p,a}}{i_{p,c}}$	$\frac{i_{p,c}\ (2)}{i_{p,c}\ (1)}$
2,2′-Azopyridine	−1.42	−1.35	0.92	−1.82	−1.70 [b]	*c*	0.34
3,3′-Azopyridine	−1.51	−1.44	0.84	−2.10	−1.95 [b]	*c*	0.65
4,4′-Azopyridine	−1.24	−1.17	0.97	−1.86	−1.75 [b]	0.74	0.76
2-Phenylazopyridine	−1.61	−1.51	0.93	−2.09	−1.85 [b]	*c*	0.64
3-Phenylazopyridine	−1.66	−1.58	0.92	−2.17	−2.00 [b]	0.49	0.73
4-Phenylazopyridine	−1.51	−1.42	0.94	−1.98	−1.80 [b]	0.68	0.67

Conditions: 2 mM substrate in 0.1M-Et_4NBF_4–CH_3CN; *v* 250 mV s^{-1}; hanging mercury drop electrode.
[a] V *vs.* Ag–0.1M-$AgNO_3$–CH_3CN. [b] Broad anodic peak. [c] Not determined.

while that of 4,4′-azopyridine became reversible at room temperature merely by passing the electrolyte solution twice through a column of activated alumina (platinum disc electrode; *v* 225 mV s^{-1}). The differences between the cathodic peak potentials of the two reversible electron transfers ($\Delta E_{p,c}$) under these conditions were 0.80 V for azobenzene (−10 °C) (lit.,[12d] *ca.* 0.8 V in DMF–Bu_4NBF_4), 0.73 V for 2,2′-azopyridine (5 °C), 0.73 V for 4,4′-azopyridine (20 °C), 0.76 V for benzophenone (−30 °C) (lit.,[12b] 0.77 V in DMF–Me_4NBr at 20 °C), and 0.51 V for perylene (5 °C) (lit.,[12c] 0.545 V in DMF—Et_4NI at 11 °C).

The addition of 1—2 mol. equiv. of dry CH_3CN to the solution of azobenzene in DMF–0.1M-Et_4NBF_4–alumina at 5 °C caused the anodic peak of the second electron transfer to disappear and brought about an anodic shift of the cathodic peak of *ca.* 0.1 V; there was no new anodic peak at less negative potential, and the original anodic peak did not reappear on lowering the temperature further. Similar behaviour was observed on adding $PhCH_2CO_2Et$ (pK_a 17),[15] but in this case a new anodic peak appeared at *ca.* 0.9 V anodic of the first electron transfer as previously reported.[6] The behaviour of 2,2′-azopyridine in a comparable set of experiments was broadly similar to that of azobenzene. At 5 °C in DMF–0.1M-Et_4NBF_4–alumina it exhibited two reversible electron transfers separated by 0.73 V, with a small additional anodic peak (A) *ca.* 0.25 V less cathodic than the first electron transfer, which was only present when the cathodic sweep extended to the second electron transfer. On raising the temperature to 22 °C, $\Delta E_{p,c}$ decreased slightly (0.715 V), the anodic peak for the second electron transfer decreased markedly, and peak (A) increased. The addition of 1 mol. equiv. of dry CH_3CN at 5 °C also caused a large decrease in the anodic peak for the second electron transfer and enhancement of peak (A), but in addition caused the appearance of a further anodic peak (B) *ca.* 0.35 V less cathodic than the first electron transfer. The addition of $PhCH_2CO_2Et$ (0.25 vol%) produced changes similar to those observed with CH_3CN, but now peak (B) was *ca.* 0.55 V less cathodic than the first electron transfer. Lowering the temperature to −50 °C produced no major change but peak (B) was now more prominent, and the anodic peak of the first electron transfer was significantly diminished; both peaks (A) and (B) increased in size relative to $i_{p,c}$ (1) as the sweep rate was increased with $i_{p,a}$ (B) increasing faster than $i_{p,a}$ (A). {For *v* = 54, 227, and 1 000 mV s^{-1}, $i_{p,a}$ (A) + $i_{p,a}$ (B)]/$i_{p,c}$ (1) and $i_{p,a}$ (B)/$i_{p,a}$ (A) were 0.29, 0.46, and 0.59, and 0.25, 0.39, and 0.67 respectively.} The addition of activated alumina to CH_3CN containing 0.1M-Et_4NBF_4 did not make the second electron transfer of either azobenzene or 2,2′-azopyridine reversible, even at reduced temperatures.

The foregoing observations lead us to the conclusion that the dianions of azobenzene and 2,2′-azopyridine, and most probably those of all of the other azopyridines and phenylazopyridines, are monoprotonated by CH_3CN. The dianion of azobenzene is clearly not available for reoxidation when CH_3CN or $PhCH_2CO_2Et$ is present in an otherwise aprotic medium. The monoprotonated dianion is known [2] to be reoxidised to azobenzene in a two-electron transfer at the same potential as the first electron transfer to azobenzene and would not therefore produce a new anodic peak, while oxidation of the conjugate base of the proton donor would give a new anodic peak in the case of $PhCH_2CO_2Et$ but not CH_3CN, at least not in the voltage range covered. Likewise for the dianion of 2,2′-azopyridine, CH_3CN and $PhCH_2CO_2Et$ significantly reduce the amount of dianion available for reoxidation. In this case however protonation could occur on the pyridyl nitrogen atoms as well as on the azo nitrogen atoms, and this, in combination with possibilities for geometrical isomerism in the ring-protonated species, could generate more than one monoprotonated dianion, with possibly different oxidation potentials. From the variable temperature and variable sweep measurements peaks (A) and (B) certainly appear to be due to oxidation of unstable species, although the position of peak (B) when $PhCH_2CO_2Et$ is used as the proton donor roughly corresponds with that assigned to the oxidation of the conjugate base of $PhCH_2CO_2Et$ (see foregoing discussion and ref. 6). For 4,4′-azopyridine, the anodic peaks generated by reduction to the dianion were those for reoxidation of the monoprotonated dianion to the parent azopyridine, at the same potential as the first electron transfer to the azopyridine, and for oxidation of 4-pyridylhydrazine (only observed in longer time-scale experiments); there was no suggestion that protonation of the dianion occurred at positions other than the azo nitrogen atoms.[2] However the 4,4′-azopyridine system lacks the ability to hydrogen-bond intramolecularly in a manner which should be possible with the 2,2′-azopyridine system.

We are therefore still confident that the reduction of azobenzene, azopyridines, and phenylazopyridines in CH_3CN serves to generate $^-CH_2CN$, and while 2,2′- and 4,4′-azopyridine and 4-phenylazopyridine considerably extend the voltage range of azo-type precursors for $^-CH_2CN$, the rate of generation of $^-CH_2CN$ from these precursors is too low for them to be of significant value in this respect.

Experimental

Acetonitrile (Fisons SLR grade) was purified and dried by the method of Forcier and Olver,[11] using the sequence (i) sodium hydride, (ii) phosphorus pentaoxide, (iii) calcium hydride, and was stored over freshly activated molecular sieves. The final water content was <100 p.p.m. (Karl Fischer titration). Dimethylformamide was dried by distillation from phosphorus pentaoxide, and was stored over freshly activated molecular sieves.

Azopyridines.—These were prepared by a literature procedure [16] which involved oxidising the appropriate aminopyri-

dine with aqueous alkaline calcium hypochlorite. The crude products were purified by dry column chromatography with ether as eluant, and were recrystallised from light petroleum (b.p. 60—80 °C). 2,2′-Azopyridine had m.p. 85—86 °C (lit.,[16] 85—86 °C), 3,3′-azopyridine had m.p. 140—141 °C (lit.,[16] 140 °C), and 4,4′-azopyridine had m.p. 108—109 °C (lit.,[16] 108—109 °C).

Phenylazopyridines.—These were prepared by a literature procedure [16] which involved condensing the appropriate aminopyridine with nitrosobenzene. The crude products were purified by dry column chromatography with either ether or ether–toluene (1 : 1) as eluant, and were recrystallised from light petroleum (b.p. 40—60 or 60—80 °C). 2-Phenylazopyridine had m.p. 30—31 °C (lit.,[16] 32—34 °C), 3-phenylazopyridine had m.p. 51—52 °C (lit.,[16] 52—53 °C), and 4-phenylazopyridine had m.p. 95—96 °C (lit.,[16] 98 °C).

Cyclic Voltammetry.—The working electrode was either a hanging mercury drop [17] or a polished platinum disc, and the reference electrode was Ag–0.1M-$AgNO_3$ in CH_3CN or DMF as appropriate. The experiments in which alumina was either added to the cell (5 g in 20 ml) or used in the form of a column, were performed essentially as described by Parker and his co-workers.[12] The best results were obtained when the alumina (ICN Pharmaceuticals, W200 neutral grade Super 1) was freshly activated by heating at 325 °C *in vacuo* for several hours and allowed to cool before dry nitrogen was admitted to the evacuated system.

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