The Use of Linear Sweep Voltammetry to study the Addition of Electrogenerated $^{-}CH_2CN$ to Aromatic Carbonyl Compounds †

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A general electroanalytical method for studying the rate of reaction between an electrogenerated species, *e.g.* nucleophile, base, electrophile, acid, or radical and an electroactive substrate is described. The method has been used to study the addition of electrogenerated $^{-}CH_2CN$ to aromatic carbonyl compounds. The cyanomethyl anion has been generated in two ways, (i) by reduction of azobenzene in acetonitrile, which involves protonation of the dianion by the solvent, and (ii) by reduction of cyanomethyltriphenyl-phosphonium and -arsonium cations in dimethylformamide, which involves reductive cleavage. A computer simulation of the electroanalytical experiments is described and representative results are given, including estimates of the rate constants for the addition of $^{-}CH_2CN$ to a series of alkyl phenyl ketones.

In 1974, we reported[1] that the electroreduction 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 $^{-}CH_2CN$ to the carbonyl group to form a hydroxynitrile (II). The nucleophile might be formed initially *via* reduction of the carbonyl compound, but subsequently it would be generated *via* the reduction of the intermediate αβ-unsaturated nitrile (III) to give the propiononitrile and hydro-dimer. The glutaronitrile is formed by Michael addition of $^{-}CH_2CN$ to the αβ-unsaturated nitrile.

In order to provide further support for our proposed reaction mechanism, we embarked upon a study of the two addition steps in the Scheme, using electroanalytical experiments in which the nucleophile, $^{-}CH_2CN$, was

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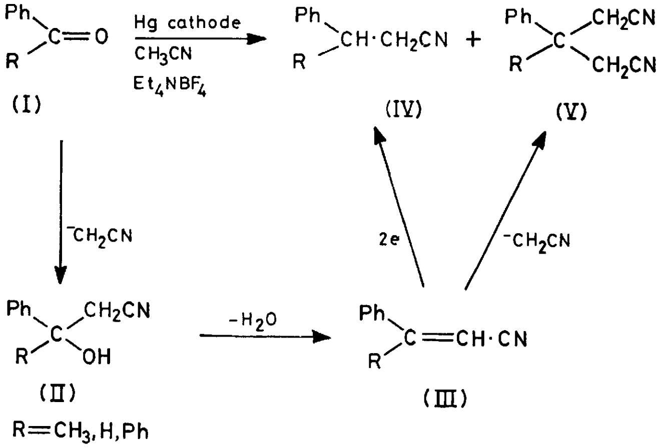
† No reprints available.

[1] E. M. Abbot, A. J. Bellamy, and J. Kerr, *Chem. and Ind.*, **1974**, 828.

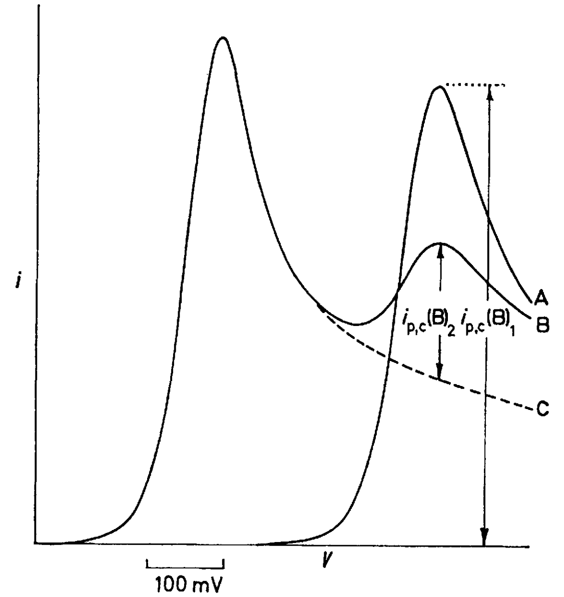
[2] A. Uchida, S. Saito, and S. Matsuda, *Bull. Chem. Soc. Japan*, 1969, **42**, 2989; E. M. Kaiser and C. R. Hauser, *J. Org. Chem.*, 1968, **33**, 3402; C. Ivanov and Y. Anghelova, *Compt. rend. Acad. bulg. Sci.*, 1966, **19**, 739.

generated electrochemically in the presence of either an aromatic carbonyl compound or corresponding unsaturated nitrile. The present paper describes results relating to the carbonyl addition.[3]



SCHEME

The basis of the electroanalytical method involves recording the linear sweep voltammogram of the carbonyl compound alone (Figure, curve A) and then in the presence of a more easily reduced compound (Figure, curve B), the reduction of which generates, either directly or indirectly, $^-CH_2CN$. Thus $^-CH_2CN$ is formed at, or close to, the electrode and reacts with the carbonyl compound. By the time the linear sweep reaches the potential necessary for reduction of the carbonyl compound, some of the latter will have been converted into the non-reducible adduct and thus the peak current for the first electron transfer of the carbonyl compound will be less than in the original sweep. The magnitude of the decrease in $i_{p,c}$ can then be used to determine the rate constant of the addition step (k_2). Apart from the rate constant for the carbonyl addition, the decrease in $i_{p,c}$ is dependent upon several other factors, the most important being the absolute and relative concentrations of the carbonyl compound and the $^-CH_2CN$ precursor, the rate at which the reduced precursor liberates $^-CH_2CN$, k_1, the difference in $E°$ between the two compounds ($\Delta E°$), and the rate at which the voltage is increased (v). The latter two factors determine the time scale of the experiment, increasing $\Delta E°$ and/or decreasing v producing a larger decrease in $i_{p,c}$, while decreasing $\Delta E°$ and/or increasing v producing a smaller decrease in $i_{p,c}$, for given values of k_1 and k_2. Obviously the electroanalytical method is a general one and may be used to study the rate of reaction between any electrogenerated species, *e.g.* nucleophile, base, or even electrophile, acid, or radical, and an electroactive substrate.



Computer simulated linear sweep voltammogram of 2mM-carbonyl compound (curve A) + 2mM-precursor for $^-CH_2CN$ (curve B): $\Delta E°$ 0.25 V; sweep rate 0.25 V s^{-1}. Rate constant for formation of $^-CH_2CN$ from reduced precursor 97 s^{-1}; rate constant for reaction of $^-CH_2CN$ with carbonyl compound 8×10^3 l mol^{-1} s^{-1}; percentage decrease in $i_{p,c}$ of carbonyl compound $100\,[i_{p,c}(B)_1 - i_{p,c}(B)_2]/i_{p,c}(B)_1 = 70\%$

Perhaps the simplest way of generating $^-CH_2CN$ electrochemically is *via* protonation of a reduced species by acetonitrile, the latter being used as the solvent. It has been shown[4] that the reduction of azobenzene in acetonitrile involves two reversible one-electron transfer steps, the radical-anion being stable but the dianion being rapidly protonated by the solvent to give the conjugate base of hydrazobenzene and the cyanomethyl anion ($^-CH_2CN$). Since the second electron transfer to azobenzene occurs at a less negative potential than the first electron transfer for many of the carbonyl compounds we wished to study, the reduction of azobenzene in acetonitrile appeared suitable for the generation of $^-CH_2CN$ in the type of electroanalytical experiment outlined above. The reduced form(s) of azobenzene has been previously used as an electrogenerated base for Michael additions,[5] and for Wittig reactions,[6] and the basicity *versus* nucleophilicity of azobenzene dianion has also been studied.[7]

When an equimolar amount of azobenzene [$E_{p,c}$ (2) −2.18 V] was added to a 2mM solution of acetophenone [$E_{p,c}$ (1) −2.45 V] in acetonitrile the peak current for acetophenone was only 25% of the corresponding peak current measured before the addition of azobenzene, *i.e.* reaction with the generated $^-CH_2CN$ gave a 75% reduction in $i_{p,c}$ (Table 1) (*cf.* 55% decrease reported in ref. 3; the conditions used to obtain the present result are considered to be more carefully controlled than those used previously). Increasing the sweep rate from 214 mV s^{-1} to 25 V s^{-1} considerably increased $i_{p,c}$ for acetophenone relative to that for

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[3] Preliminary communication, A. J. Bellamy, *J.C.S. Chem. Comm.*, 1975, 944.

[4] K. G. Boto and F. G. Thomas, *Austral. J. Chem.*, 1973, **26**, 1251.

[5] M. M. Baizer, J. L. Chruma, and D. A. White, *Tetrahedron Letters*, 1973, 5209.

[6] P. E. Iversen and H. Lund, *Tetrahedron Letters*, 1969, 3523.

[7] T. Troll and M. M. Baizer, *Electrochim. Acta*, 1975, **20**, 33.

azobenzene due to the shorter time available for the chemical reaction. Similarly, when an equimolar amount of azobenzene was added to a 2mM solution of benzophenone [$E_{p,c}$ (1) -2.19 V] in acetonitrile, the $i_{p,c}$ of the latter was decreased by 70% (Table 1). In this latter 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; this ratio was found to be unchanged in the presence of acetophenone.

TABLE 1

Ketone ($E_{p,c}$/V *versus* Ag–Ag$^+$)	% decrease in $i_{p,c}$ of ketone on addition of azobenzene	Approx. k_2^{a}/l mol^{-1} s^{-1}
Acetophenone(-2.45)	75	16 000
Propiophenone (-2.48)	85	>51 000
Isopropyl phenyl ketone (-2.50)	36	630
Benzoylcyclopropane (-2.49)	22	280
Phenyl t-butyl ketone (-2.54)	14	160
Acetylmesitylene (-2.85)	39	200 ^{b}
Benzophenone (-2.19)	70	*c*
Indan-1-one. (-2.48)	*ca.* 100	*d*

Ketone (2mM) + azobenzene (2mM) in 0.1M-Et_4NBF_4–CH_3CN; hanging mercury drop; sweep rate 214 mV s^{-1}.

[a] Assumptions: no regeneration of $^-CH_2CN$, rate constant for protonation of azobenzene dianion 97 s^{-1}, $\Delta E°$ 0.25 V, v 0.25 V s^{-1}. [b] $\Delta E°$ 0.75 V. [c] $\Delta E°$ *ca.* 0. [d] Regeneration of $^-CH_2CN$ known to be occurring.

If the interpretation of the decrease in $i_{p,c}$ for acetophenone and benzophenone on addition of azobenzene is correct, then changing the solvent from acetonitrile to dimethylformamide could reasonably be expected to produce no decrease in $i_{p,c}$. For the control experiments in dimethylformamide, azobenzene could not be used because its $E_{p,c}$ (2) is too cathodic in this solvent, *i.e.* more cathodic than $E_{p,c}$ (1) of benzophenone. Therefore 2,2′-azonaphthalene was substituted for azobenzene in the dimethylformamide experiments since it is reduced at less negative potentials [8] but exhibits similar electrochemical behaviour to azobenzene in both dimethylformamide [8] and acetonitrile. Unfortunately, 2,2′-azonaphthalene has a low solubility in acetonitrile, and thus the same azo-compound could not be used in both solvents.

As anticipated the addition of an equimolar amount of 2,2′-azonapahthalene [$E_{p,c}$ (2) -2.28 V] to a 2mM solution of benzophenone [$E_{p,c}$ (1) -2.28 V] in dimethylformamide produced no decrease in the $i_{p,c}$ of benzophenone, but a similar experiment with acetophenone [$E_{p,c}$ (1) -2.54 V] produced a decrease of 40%. A possible explanation for this latter result is that acetophenone could react *via* deprotonation by the 2,2′-azonaphthalene dianion or some intermediate base; this mode of reaction is impossible for benzophenone. However, when the experiment was repeated using [$^2H_3$]acetophenone the decrease (37%) was the same within experimental error; a primary kinetic isotope effect for the deprotonation step of only 2 would reduce the percentage decrease to *ca.* 25%.[9] Thus the cause of the decrease with acetophenone in dimethylformamide is uncertain. The absence of any decrease for benzophenone indicates that nucleophilic addition of the dianion of the azo-compound [7] 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 addition of $^-CH_2CN$ to the carbonyl group may be only partly responsible for the decrease.

A further change which was observed when azobenzene was added to acetophenone in acetonitrile was that the cyclic voltammogram of acetophenone changed from being partially irreversible ($i_{p,a}/i_{p,c}$ 0.59; τ 0.55 s) [10] to being almost completely reversible; similar behaviour was observed with propiophenone. This behaviour can be attributed to a lowering of the water content of the solvent close to the electrode as follows. The partial irreversibility of the cyclic voltammogram of acetophenone is due to dimerisation of the radical-anion, and the rate constant for the dimerisation step has been shown [11] to vary with the water content of the solvent, being 1.3×10^6 for 5.3% water, 4×10^5 for 1.3% water, and 3×10^4 l mol^{-1} s^{-1} for 0.3% water in acetonitrile. This has been attributed to solvation of the radical-anion by water reducing the coulombic repulsion between radical-anions. In our own experiments, the water content of the acetonitrile was 0.01% with an estimated dimerisation rate constant of 2×10^3 l mol^{-1} s^{-1}. Extrapolation of these data to lower water levels indicates that reversible cyclic voltammetry behaviour would be observed (k_{dim} 125 l mol^{-1} s^{-1}) for a water content of *ca.* 0.003%, and it seems reasonable that this condition would be achieved in the vicinity of the electrode due to scavenging of residual water by the strong bases formed on reduction of azobenzene.*

The results for other carbonyl compounds using azobenzene in acetonitrile are given in Table 1. As the carbonyl group of a series of alkyl phenyl ketones becomes more crowded the percentage decrease falls off, as would be expected for a carbonyl addition reaction. The result for indan-1-one is particularly significant; the reduction peak almost entirely disappeared for a solution 2mM in both components. At higher concentrations of indan-1-one (4 and 6mM) but still using 2mM-azobenzene, the decreases were 75 and 61%, respectively. If the $^-CH_2CN$ generated by reduction of each molecule of azobenzene were capable of reacting with only one molecule of the carbonyl compound, the maximum decrease expected for these two cases would be 50 and 33% respectively. The results for indan-1-one

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* We thank Professor J. M. Saveant for helpful discussions on this point.

[8] J. L. Sadler and A. J. Bard, *J. Amer. Chem. Soc.*, 1968, **90**, 1979.

[9] A. J. Bellamy, G. Howat, and I. S. MacKirdy, unpublished calculations.

[10] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

[11] J. M. Saveant and D. Tessier, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1975, **61**, 251.

therefore indicate that on average more than one equivalent of the ketone is being converted to a non-reducible form for each $^{-}CH_2CN$ initially generated. This could arise as follows: the initial adduct, an oxy-anion, could abstract a proton from the acetonitrile thus regenerating $^{-}CH_2CN$, which could then either add to or abstract a proton from another indan-1-one molecule. In view of the result with [$^2H_3$]acetophenone in dimethylformamide, deprotonation appears the least likely route. Obviously, the regeneration of $^{-}CH_2CN$ may also operate with the other carbonyl compounds, and thus contribute to the decreases observed.

Since the second electron transfer to azobenzene occurs at a potential ($E_{p,c}$ −2.18 V) which limits the study of the more readily reducible carbonyl compounds [*cf.* benzophenone ($E_{p,c}$ −2.19 V)] and unsaturated nitriles we have investigated the use of other, more easily reduced azo-compounds as sources of $^{-}CH_2CN$, particularly azopyridines. The electroanalytical behaviour of 4,4′-azopyridine in dimethylformamide had already been studied[8] and the reported $E_{p,c}$ values indicated that a study of the isomeric azopyridines, as well as the isomeric benzeneazopyridines, might be rewarding. However, when reduction to the dianion occurs at a less negative potential, it usually follows that the dianion is more stable and does not protonate as rapidly as the dianion of azobenzene. This is certainly the case for 4,4′-azopyridine [$E_{p,c}$ (2) −1.86 V], which has a less irreversible second electron transfer in acetonitrile than azobenzene,[12] and for 4-nitroazobenzene [$E_{p,c}$ (2) −1.195 V *versus* s.c.e.], which exhibits a reversible second electron transfer in acetonitrile.[13] The lower rate of protonation of the dianion of 4,4′-azopyridine in acetonitrile is reflected in a lower percentage decrease in the $i_{p,c}$ of benzophenone compared with the decrease observed with azobenzene.[12] The electroanalytical behaviour of the isomeric azopyridines and benzeneazopyridines, and their use as precursors for $^{-}CH_2CN$ will be reported later.

In order to avoid the complication of a $^{-}CH_2CN$ regeneration process, we have looked at the possibility of generating $^{-}CH_2CN$ by a reductive cleavage reaction since this could be used in other solvents, particularly dimethylformamide. By working in dimethylformamide, proton abstraction from the medium by an intermediate base would not regenerate $^{-}CH_2CN$ and the study of the initial addition step would be simplified. Three potential precursors have been studied, cyanomethyltriethylammonium iodide (VI), cyanomethyltriphenylphosphonium bromide (VII), and cyanomethyltriphenylarsonium bromide (VIII). The ammonium salt is unsatisfactory because $E_{p,c}$ for one electron reduction is too high (−2.47 V). The phosphonium salt ($E_{p,c}$ −1.95 V) has previously been used by Wagenknecht and Baizer[14] for the same purpose in dimethyl sulphoxide. The electrochemical behaviour of the arsonium salt has not previously been studied.

$Et_3\overset{+}{N}CH_2CN\ I^-$ (VI) $Ph_3\overset{+}{P}CH_2CN\ Br^-$ (VII) $Ph_3\overset{+}{As}CH_2CN\ Br^-$ (VIII)

The reduction of the cyanomethyltriphenylphosphonium cation has been shown[14] to involve the transfer of two electrons at the first reduction peak, generating Ph_3P and $^{-}CH_2CN$. $^{-}CH_2CN$ then rapidly abstracts a proton from another parent cation forming the ylide. Two electrons are therefore transferred with the consumption of two mols of the cation, the deprotonation being sufficiently rapid to produce a pseudo one-electron transfer peak on linear sweep voltammetry (v 214 mV s^{-1}). A second reduction peak is observed at $E_{p,c}$ −2.85 V, this being attributed to reduction of the ylide formed as a result of the first reduction process. The electrochemical behaviour of the cyanomethyltriphenylphosphonium cation in acetonitrile is almost identical to that of the phenacyltriphenylphosphonium cation in acetonitrile,[15] except that while the non-ylide product formed in the deprotonation step in the latter case, *viz.* acetophenone, is electroactive, the corresponding product in the former case, *viz.* acetonitrile, is electro-inactive.

The electrochemical behaviour of the cyanomethyltriphenylarsonium cation is similar to that of the phosphorus analogue, the linear sweep voltammogram exhibiting a pseudo-one-electron reduction peak at $E_{p,c}$ −1.70 V and a further reduction peak at $E_{p,c}$ −2.55 V. The pK_a of the arsonium cation would be expected to be only 2—3 units above that of the phosphonium cation (*cf.* pK_a of $Ph_3\overset{+}{As}CH_2COPh$ is *ca.* 2.5 units above the pK_a of $Ph_3\overset{+}{P}CH_2COPh$ in aqueous ethanol[16]) and therefore would also be expected to be rapidly deprotonated by $^{-}CH_2CN$ (pK_a CH_3CN 25)[17] to form the ylide. However, the first reduction peak is less electrochemically reversible ($E_p - E_{p/2}$ 110 mV) than the phosphorus analogue ($E_p - E_{p/2}$ 60 mV), and is therefore less satisfactory as a precursor for $^{-}CH_2CN$ from the aspects of experimental reproducibility and mathematical modelling. Both cations are non-ideal in that they will compete with the carbonyl compound for reaction with the generated $^{-}CH_2CN$, but this problem may be more amenable to study than the original one of $^{-}CH_2CN$ regeneration.

The addition of equimolar and twice equimolar amounts of cyanomethyltriphenylphosphonium bromide to a 2mM solution of benzophenone ($E_{p,c}$ −2.28 V) in dimethylformamide gave decreases in $i_{p,c}$ of the ketone of 31 and 60% respectively,* while corresponding

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* A control experiment in which a 2mM solution of benzophenone was treated with an equimolar amount of the ylide derived from the cyanomethyltriphenylphosphonium cation showed no change in the concentration of the ketone after 1.5 h.

[12] A. J. Bellamy, I. S. MacKirdy, and K. Niven, unpublished results.

[13] K. G. Boto and F. G. Thomas, *Austral. J. Chem.*, 1971, **24**, 975.

[14] J. H. Wagenknecht and M. M. Baizer, *J. Org. Chem.*, 1966, **31**, 3885.

[15] J. M. Saveant and S. K. Binh, *Bull. Soc. chim. France*, 1972, 3549.

[16] G. Aksnes and J. Songstad, *Acta Chem. Scand.*, 1964, **18**, 655.

[17] R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

amounts of cyanomethyltriphenylarsonium bromide added to the same ketone solution gave decreases of 15 and 31% respectively. The addition of an equimolar amount of cyanomethyltriphenylphosphonium bromide to a 2mM solution of indan-1-one ($E_{p,c}$ −2.54 V) in dimethylformamide gave a decrease of 23%. The decreases observed in these experiments are significantly less than those found using azobenzene in acetonitrile, and this is presumably due in part to the elimination of the $^-CH_2CN$ regeneration process. The smaller decreases observed with benzophenone in the presence of the arsonium precursor compared with those with the phosphonium precursor may be due to a larger kinetic acidity of the former cation, even though the thermodyanamic acidities are expected to be in the reverse order, making it a more effective competitor for the available $^-CH_2CN$. Since some of the $^-CH_2CN$ is being removed from the kinetic system by reaction with the carbonyl compound, it might have been anticipated that the $i_{p,c}$ for the $^-CH_2CN$ precursor would increase in the presence of the carbonyl compound, since less ylide formation might occur and therefore more cation would be available for reduction. However this is not observed to a significant extent, presumably because the adduct formed between $^-CH_2CN$ and the carbonyl compound, an oxyanion, would still be capable of deprotonating the cation and generating ylide.

Computer Simulation of the Electroanalytical Experiments and Estimation of k$_2$ *Values*.—The model system may be written as (a)—(d) in which species A is the

$$A + e \rightleftharpoons A^- \qquad (a)$$

$$A^- \xrightarrow{k_1} Z \qquad (b)$$

$$B + e \rightleftharpoons B^- \qquad (c)$$

$$B + Z \xrightarrow{k_2} Y \qquad (d)$$

precursor for the generation of $^-CH_2CN$, *e.g.* azobenzene radical-anion or cyanomethyl 'onium cation, B is the reactive substrate *e.g.* carbonyl compound, Z is the reactive intermediate *e.g.* $^-CH_2CN$, and Y is the electro-inactive product from the reaction of B with Z; k_1 is the rate constant for the formation of Z ($^-CH_2CN$) from the reduced form of the precursor A (pseudo-first order for the case of proton abstraction from acetonitrile by the azobenzene dianion), and k_2 is the rate constant for the reaction of B with Z (second order). We have assumed that both electron transfer steps are reversible, and that both chemical steps are irreversible.

The relevant equations for diffusion and chemical reaction are (1a—e) with the concentrations of each species being a function of both distance from the electrode surface, x, and time, t, *e.g.* $C_A \equiv C_A(x, t)$. The boundary conditions to be satisfied by each concentration variable are given by (2)—(4) where $C_A{}^b$ and $C_B{}^b$ are the bulk concentrations of A and B respectively. Since the electron transfer steps are assumed to be reversible, the Nernst equation may be applied to the concentrations of species A, A$^-$, B, and B$^-$ at the electrode surface [equation (5) where E_t is the applied potential at time t, which for a linear sweep equals $E_0 - vt$, with E_0 being the initial potential and v being the sweep rate in V s^{-1}].

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} \qquad (1a)$$

$$\frac{\partial C_{A^-}}{\partial t} = D_{A^-} \frac{\partial^2 C_{A^-}}{\partial x^2} - k_1 C_{A^-} \qquad (1b)$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} - k_2 C_B C_Z \qquad (1c)$$

$$\frac{\partial C_{B^-}}{\partial t} = D_{B^-} \frac{\partial^2 C_{B^-}}{\partial x^2} \qquad (1d)$$

$$\frac{\partial C_Z}{\partial t} = D_Z \frac{\partial^2 C_Z}{\partial x^2} - k_2 C_B C_Z + k_1 C_{A^-} \qquad (1e)$$

(i) $t = 0$
$C_A(x, 0) = C_A{}^b$
$C_B(x, 0) = C_B{}^b$
$C_Z(x, 0) = C_{A^-}(x, 0) = C_{B^-}(x, 0) = 0$ (2)

(ii) $t > 0,\ x \longrightarrow \infty$
$C_A(x, t) = C_A{}^b$
$C_B(x, t) = C_B{}^b$
$C_Z(x, t) = C_{A^-}(x, t) = C_{B^-}(x, t) = 0$ (3)

(iii) $t > 0,\ x = 0$

$$D_A \left.\frac{\partial C_A}{\partial x}\right|_{x=0} = -D_{A^-} \left.\frac{\partial C_{A^-}}{\partial x}\right|_{x=0} \qquad (4a)$$

$$D_B \left.\frac{\partial C_B}{\partial x}\right|_{x=0} = -D_{B^-} \left.\frac{\partial C_{B^-}}{\partial x}\right|_{x=0} \qquad (4b)$$

$$D_Z \left.\frac{\delta C_Z}{\partial x}\right|_{x=0} = 0 \qquad (4c)$$

$$C_A(0, t)/C_{A^-}(0, t) = \exp\left[F(E_t - E_A{}^\circ)/RT\right] \qquad (5a)$$

$$C_B(0, t)/C_{B^-}(0, t) = \exp\left[F(E_t - E_B{}^\circ)/RT\right] \qquad (5b)$$

After solving the equations, the total current at any time may be calculated from equation (6) where s is the electrode area. The contribution to the current by reduction of B only may be calculated from (7).

$$i_{\text{total}} = Fs\left[D_A \left.\frac{\partial C_A}{\partial x}\right|_{x=0} + D_B \left.\frac{\partial C_B}{\partial x}\right|_{x=0}\right] \qquad (6)$$

$$i_B = FsD_B \left.\frac{\partial C_B}{\partial x}\right|_{x=0} \qquad (7)$$

These equations were solved numerically using the so-called explicit, finite difference method.[18] The total time for the potential sweep is divided into small segments, Δt, and the derivative $\partial C_{A^-}/\partial t$, for example, is replaced by expression (8). Similarly, the variable x is partitioned into segments, Δx, ensuring that the maximum distance from the electrode is greater than the

$$[C_{A^-}(x, t + \Delta t) - C_{A^-}(x, t)/\Delta t] \qquad (8)$$

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[18] I. S. Berezin and N. P. Zhidkov, 'Computing Methods,' Pergamon, Oxford, 1965, vol. 2, pp. 526*ff*.

maximum diffusion layer thickness. The second-order partial derivative $\partial^2 C_{A^-}/\partial x^2$, for example, is then replaced by expression (9). Combining equations (8) and (9), the

$$\frac{C_{A^-}(x + \Delta x, t) - 2\,C_{A^-}(x, t) + C_{A^-}(x - \Delta x, t)}{(\Delta x)^2} \qquad (9)$$

difference scheme to be employed in solving equation (1b) is then (10). Thus, the concentration $C_{A^-}(x, t + \Delta t)$ is

$$C_{A^-}(x, t + \Delta t) = (1 - k_1\Delta t)C_{A^-}(x, t) + \frac{D_{A^-}\Delta t}{(\Delta x)^2}[C_{A^-}(x + \Delta x, t) - 2C_{A^-}(x, t) + C_{A^-}(x - \Delta x, t)] \qquad (10)$$

obtained from the known concentrations at time t using equation (10). The numerical solution is initiated at E_0 using boundary condition 2. Since we have ensured that the computation commences outside the diffusion layer, boundary condition 3 is imposed and the computation proceeds inwards towards the electrode. This procedure is continued up to the first point out from $x = 0$. At this stage it is necessary to apply boundary conditions 4 and 5. From pilot calculations it was found necessary to calculate the derivative at $x = 0$ by at least a six-point Langrangian formula.[19] Thus, assuming the diffusion coefficients of A and A^- to be identical, equation (4a) yields (11) where $\{L_i\}$ are the

$$C_A(0, t + \Delta t) + C_{A^-}(0, t + \Delta t) = -\frac{1}{L_0}\sum_{i=1}^{5} L_i[C_A(n\Delta x, t + \Delta t) + C_{A^-}(n\Delta x, t + \Delta t)] \qquad (11)$$

Langrange coefficients. Using equation (5a) one can compute $C_A(0, t + \Delta t)$ and $C_{A^-}(0, t + \Delta t)$ and proceed to obtain the current due to the A/A^- redox system. The current due to the B/B^- redox system is computed in a similar manner. Having reached $x = 0$, the time and applied potential are now incremented and the whole computation repeated until the entire voltammogram has been constructed.

The method employed here, based on equation (8), the so-called 'explicit solution', is easy to employ but suffers from the limitation that equation (10) is stable only when $D_A - \Delta t/(\Delta x)^2 \leqslant \frac{1}{2}$ (for $k_1 = 0$);[18] obviously a choice of Δx dictates the upper limit of Δt. In order to represent adequately the second-order partial derivative by equation (9), a small Δx is desirable, thus forcing a choice of Δt which may be smaller than necessary to represent adequately the derivative in equation (8); this results in more computing time.

The problem of choosing a suitable mesh Δx is facilitated if one makes use of the results obtained previously by Nicholson and Shain.[10] For example, setting $k_2 = 0$ effectively decouples the A and B systems, the first being reduction followed by chemical reaction (e.c.) and the second being a reversible reduction. The choice of grid is then one which reproduces previous calculations [10] to a satisfactory accuracy.

In order to test the simulation procedure, the following values were selected: v −0.25 V s^{-1}, $C_A{}^b = C_B{}^b =$ 2mM, E_0 −2.000 V, $E_A{}^0$ −2.190 V, $E_B{}^0$ −2.442 V, all diffusion coefficients 2×10^{-5} cm^2 s^{-1}, diffusion layer thickness 0.039 cm, sweep time 4 s, 93 and 1 200 points in x and t respectively. The following cases were investigated: (i) k_1 and k_2 set to zero, producing two independent, reversible, redox systems, (ii) k_1 set to 97.357 s^{-1} and k_2 to 0, producing an e.c. system for A. The value for k_1 (97.357 s^{-1}) corresponds, for a sweep rate of 0.25 V s^{-1}, to a k_f/a value of 10 in the Nicholson and Shain [10] treatment of an e.c. system; the latter gave a cyclic voltammogram which closely resembled that of the second electron transfer of azobenzene in acetonitrile. The results obtained from these calculations were in good agreement with those of Nicholson and Shain [10] for both the reversible, redox system and the e.c. system, and indicated that coupling the A and B systems by introducing non-zero values for k_2 should give reliable results.

Some representative results which demonstrate the dependence of the peak current for reduction of B [$i_{p,c}$ (B)] upon (i) the sweep rate v, (ii) the difference in $E°$ for the A/A^- and B/B^- redox systems, $\Delta E°$, (iii) the concentrations of A and B, $C_A{}^b$ and $C_B{}^b$, (iv) k_1, and (v) k_2, expressed as a percentage decrease from the peak current for reduction of B when $k_2 = 0$, are given in Table 2. From these data we observe that (a) as the time interval for the reaction of Z with B is decreased, either by increasing v or by decreasing $\Delta E°$, there is a drop in the percentage decrease in $i_{p,c}$ (B); (b) as the rate of generation of Z from A^- is increased, the percentage decrease in $i_{p,c}$ (B) also increases initially, but above k_1 10 s^{-1} any further change is small; (c) above k_2 2 000 l mol^{-1} s^{-1} further increases in k_2 have a progressively smaller effect. [As k_2 increases from 0 to 51 200 l mol^{-1} s^{-1}, there is a small cathodic shift in $E_{p,c}$ (B) (16 mV)]. The simulation is unstable at k_1 200 s^{-1} and at k_2 10^5 l mol^{-1} s^{-1}, and should it become necessary to use higher values of k_1 and k_2 we shall need to use a finer mesh, and hence more computing time.

From the calculations with variation of k_2 it appears that the experimental result for the indan-1-one–azobenzene–acetonitrile system (*ca.* 100% decrease) could never be achieved using this reaction scheme and realistic values of k_2. However, if the simulation is extended to include a catalytic process (e) which would correspond

$$Y \xrightarrow{k_3} Z \qquad (e)$$

to proton abstraction from the solvent by the initial adduct, an oxyanion, and k_3 is set equal to k_1 (97.357 s^{-1}) with k_2 6 000 l mol^{-1} s^{-1}, the percentage decrease in $i_{p,c}$ (B) is increased from 67.9 to 99.0%. [When the catalytic process is incorporated, the calculated percentage decrease in $i_{p,c}$ (B) is probably fairly insensitive to the value of k_2]. Thus, the regeneration of $^-CH_2CN$ (Z) in the indan-1-one–azobenzene–acetonitrile system is indicated by both the experimental result at concentrations of indan-1-one >2mM and by the computer simulation.

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[19] M. Abramowitz and I. A. Stegun, 'Handbook of Mathematical Functions,' Dover, New York, 1965, p. 914.

Approximate rate constants for the reaction of $^{-}CH_2CN$ with alkyl phenyl ketones (k_2) in the azobenzene–acetonitrile system are included in Table 1. These were calculated by the above simulation programme with the following assumptions: (i) no regeneration of $^{-}CH_2CN$ (no catalytic process included), (ii) the rate constant for protonation of azobenzene dianion by acetonitrile (k_1) is 97 s^{-1} (a change in k_1 by an order of magnitude either way would have only a small effect on the calculated result; see Table 2), (iii) $\Delta E°$ 0.25 V [$E_{p,c}$ (2) of azobenzene −2.18 V; since we estimate k_1 97 s^{-1}, $E°$ (2) for azobenzene will be at −2.19 V ($E_{p,c}$ is 9.8 mV anodic of $E°$ for k_f/a 10);[10] the $\Delta E°$ value of 0.25 V is a reasonable average value for all the alkyl phenyl ketones except acetylmesitylene], (iv) v 0.25 V s^{-1}. (This is slightly greater than the sweep rate actually used, but the error will be small.) We hope to improve the accuracy of these calculations by obtaining better estimates of k_1 and k_3, and by incorporating the catalytic process where appropriate.

TABLE 2

Calculated decrease in $i_{p,c}$ (B) as a function of v, $\Delta E°$, $C_A{}^b$, $C_B{}^b$, k_1, and k_2

	v/ V s^{-1}	$\Delta E°$/ V	$C_A{}^b$/ mM	$C_B{}^b$/ mM	k_1*/ s^{-1}	k_2/ l mol^{-1} s^{-1}	Decrease in $i_{p,c}$(B) (%)
v	0.10	0.40	2	2	97.357	1 200	66.5
	0.15						62.0
	0.20						58.2
	0.25						54.9
	0.30						52.0
	0.50						42.9
$\Delta E°$	0.25	0.75	2	2	97.357	1 600	66.7
		0.50					61.8
		0.25					52.4
$C_A{}^b$,$C_B{}^b$	0.25	0.25	2	2	97.357	1 600	52.4
				4			34.0
				6			24.6
			1	2		6 000	37.1
			2	4			39.7
k_1	0.25	0.25	2	2	97.357	1 600	52.5
					38.943		51.3
					15.577		49.3
					9.736		47.6
					4.868		43.3
					1.947		32.8
					0.487		13.6
k_2	0.25	0.25	2	2	97.357	51 200	81.3
						25 600	77.8
						12 800	73.6
						6 400	68.4
						3 200	61.6
						1 600	52.5
						800	40.9
						400	28.5
						200	17.7
						100	10.1
						50	5.4

All unspecified parameters had their previously assigned values

* k_1 values of 97.357 38.943 15.577, 9.736, 4.868, 1.947, and 0.487 s^{-1} correspond to k_f/a values of 10, 4.0, 1.6, 1.0, 0.5, 0.2, and 0.05 respectively.[10]

We shall not attempt to calculate k_2 for the cyanomethyl 'onium cation–dimethylformamide system in the present paper since at present we have no information on k_1 for this system or the rate constants for deprotonation of the cation by $^{-}CH_2CN$ and the oxyanion.

EXPERIMENTAL

Acetonitrile (Fisons SLR grade) was purified and dried by the method of Forcier and Olver [20] using the sequence (i) sodium hydride, (ii) phosphorus pentaoxide, (iii) calcium hydride and was stored over molecular sieve. The final water content was 0.01%. Acetonitrile as supplied by Aldrich could not be easily purified using the above procedure. Dimethylformamide was purified and dried by the method of Ritchie and Megerle,[21] and was stored over molecular sieves.

2,2′-Azonaphthalene.—This was prepared from 2-nitronaphthalene using the method of Corbett.[22] Extensive chromatography and repeated recrystallisation from toluene was required to obtain a pure product, m.p. 208.5—210 °C (lit.,[22] 208 °C).

ααα-Trideuterioacetophenone.—A mixture of acetophenone (6.0 g), deuterium oxide (20 ml), and anhydrous potassium carbonate (1 g) was refluxed for 24 h, the aqueous phase was removed and further amounts of deuterium oxide (30 ml) and anhydrous potassium carbonate (1.5 g) were added. After refluxing for a further 20 h, dry ether (50 ml) was added, the aqueous layer was removed, and the organic phase was stirred with deuterium oxide (3 ml) and a small quantity of sodium chloride. The organic phase was separated, dried over calcium chloride, concentrated, and distilled, b.p. 89 °C at 10 mmHg, to give pure ααα-trideuterioacetophenone.

The deuterium content of the ketone was found (g.l.c.–m.s.) to be unchanged after treatment with 0.1M solutions of tetraethylammonium fluoroborate in both acetonitrile and dimethylformamide for 2 h, indicating that no exchange would occur during the period required for cyclic voltammetry experiments.

Acetylmesitylene.—This was prepared by acetylation of mesitylene,[23] and was shown to be pure by g.l.c. analysis.

Cyanomethyltriethylammonium Iodide.—A solution of iodoacetonitrile (1.67 g) and triethylamine (1.21 g) in propan-1-ol (20 ml) was left to stand for 24 h before collecting the white crystalline salt, m.p. 186—187 °C (from propan-1-ol) (lit.,[24] m.p. 187 °C).

Cyanomethyltriphenylphosphonium Bromide.—The phosphonium salt was prepared by the method of Wagenknecht and Baizer,[14] and had m.p. 256—259 °C (from ethanol) (lit.,[25] 256—258 °C); $\nu_{max.}$ (Nujol) 2 250 cm^{-1}; δ([$^2H_6$]-DMSO) 6.22 (2 H, d, $J_{H,P}$ 16 Hz) and 7.9 (15 H, m); δ_C ([$^2H_6$]DMSO; H decoupled) 135.98 (s, C-4), 133.79 and 130.53 (both d, C-2 and -3), 116.21 (d, C-1), 112.86 (d, CN), and 14.92 p.p.m. (d, CH_2); *m/e* 301 (*P* − HBr), 300, 185 (Ph_2P), and 183 (no parent ion). The ylide was prepared by treatment with aqueous sodium hydroxide, m.p. 191—196 °C (from ethyl acetate) (lit.,[26] 195—196 °C).

Cyanomethyltriphenylarsonium Bromide.—A solution of bromoacetonitrile (1.31 g) and triphenylarsine (3.35 g) in nitromethane (10 ml) was heated in an oil-bath at 110 °C for 5 h. After cooling, the yellow solution was poured into

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[21] C. D. Ritchie and G. H. Megerle, *J. Amer. Chem. Soc.*, 1967, **89**, 1447.

[22] J. F. Corbett, *Chem. Comm.*, 1968, 1257.

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[24] D. B. Luten, *J. Org. Chem.*, 1938, **3**, 588.

[25] G. P. Schiemenz and H. Engelhard, *Chem. Ber.*, 1961, **94**, 578.

[26] S. Trippett and P. M. Walker, *J. Chem. Soc.*, 1959, 3874.

ether (100 ml) and the solid was filtered off, crushed, and washed with ether. The crude product (3.12 g) was redissolved in nitromethane and reprecipitated by adding ether to give a white crystalline solid (2.93 g), m.p. 194—206 °C. It was recrystallised twice more from nitromethane only to give constant m.p. 198—210 °C [lit.,[27] 210 °C (decomp.)] (Found: C, 56.0; H, 4.05; N, 3.2. Calc. for $C_{20}H_{17}AsBrN$: C, 56.35; H, 4.0; N, 3.3%). Although the m.p. had a wide range, the product appeared to be pure as shown by elemental analysis and by comparison of its spectroscopic properties with those of cyanomethyltriphenylphosphonium bromide. It had $\nu_{max.}$ (Nujol) 2 220 cm^{-1}; δ([$^2H_6$]DMSO) 5.82 (2 H, s) and 7.9 (15 H, m); δ_C ([$^2H_6$]DMSO; H decoupled) 134.74 (s, C-4), 132.89 and 130.87 (both s, C-2 and -3), 120.23 (s, C-1), 113.78 (s, CN), and 13.82 p.p.m. (s, CH_2), with similar relative intensities to those observed for cyanomethyltriphenylphosphonium bromide; *m/e* 306 (*P* — $BrCH_2CN$), 229 (Ph_2As), 227, 153, and 152 (no parent ion).

General Procedure for Electroanalytical Experiments.—The working electrode was a hanging mercury drop, the secondary electrode was platinum, and the reference electrode was Ag–0.1M-$AgNO_3$ in acetonitrile or dimethylformamide. The reference electrode solution was connected to the test solution *via* a cracked-glass seal. The voltage sweep rate was normally 214 mV s^{-1}. A 0.1M solution of tetraethylammonium fluoroborate in dry acetonitrile or dry dimethylformamide (20 ml) was added to the cell, the cell and solution were flushed with dry nitrogen, and the background voltammogram was recorded. The test substrate, *e.g.* carbonyl compound, was added to the cell as a solution (1.00 ml) in the appropriate solvent (0.2 mmol in 5.0 ml) to give a final concentration of 2mM.* After flushing with nitrogen, the linear sweep or cyclic voltammogram was recorded (Figure, curve A); the peak current for the first electron transfer was the averaged value from several runs. The precursor for the generation of $^-CH_2CN$, *e.g.* azobenzene in acetonitrile or cyanomethyltriphenylphosphonium bromide in dimethylformamide, was then added to the cell as a solution (1.00 ml) in the appropriate solvent (0.2 mmol in 5.0 ml) to give a final concentration of 2mM.* After further flushing with nitrogen, the linear sweep or cyclic voltammogram was rerecorded (Figure, curve B). In order to measure the peak current of the first electron transfer of the test substrate, the linear sweep voltammogram was recorded using the time-base of the *XY*–t recorder, first for the full voltage range and then for a limited range stopping just before the reduction peak of the test substrate. Thus an extension of the cathodic peak of the precursor was used as the base line from which to measure the peak current of the test substrate (Figure, curve C). The averaged value from several runs was obtained.

We thank the University of Edinburgh for the award of a student demonstratorship to I. S. M. and G. H. thanks I.C.I. for a Research Fellowship.

[7/1444 *Received, 8th August,* 1977]

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* These concentrations were slightly less than indicated due to the dilution involved in additions.

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