Electrochemical Reduction of Azabenzenes in Acetonitrile. Reactivity of the Diazine Radical Anion

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Abstract: The electrochemical reduction of five azabenzenes (pyridine, pyridazine, pyrimidine, pyrazine, and s-triazine) has been investigated; detailed mechanistic steps and rate constants for radical anion protonation are presented. Pyrazine and pyridazine exhibit generally similar ECE reduction mechanisms in acetonitrile: initial one-electron reversible reduction to a radical anion, which abstracts a proton from the solvent and/or residual water to produce a free radical species that is unstable at the potential of its formation and is immediately reduced in a second one-electron process. Pyridine is probably also reduced by the same general type of ECE mechanism. Addition of water generally shifts $E_{1/2}$ to more positive potential and increases the reduction current, except for s-triazine, whose current is unaffected by as much as 1% added water. Addition of acid produces a new reduction wave at less negative potential than the original reduction wave; this new wave is attributed to the reduction of a N-protonated azabenzene species. The behavior of these compounds is contrasted with that of pyrimidine and compared with that reported by other investigators.

Although considerable work has been done on the electrochemistry of nitrogen heterocyclic compounds in aqueous media,[2] most of the studies on their electrochemistry in nonaqueous media until quite recently deal primarily with radical anion generation to observe electron paramagnetic resonance (epr) spectra.[3] The need to explore valid ways for correlating electrochemical behavior with structure and reactivity, as well as the intrinsic importance of the compounds involved (e.g., the pyrimidine ring is the fundamental species involved in the reduction of many biologically important compounds of the pyrimidine–purine types), has prompted an investigation of the azabenzenes in nonaqueous media (specifically, acetonitrile) in order to examine better the initial energy-controlling one-electron step and the properties of the anion free radical generated by such a step.

The behavior of pyrimidine (1,3-diazine) in acetonitrile has been previously reported[4] and is subsequently summarized as necessary. In the present paper, the behavior of the monazine (pyridine), the other two di-

azines (1,2-pyridazine and 1,4-pyrazine), and the symmetrical triazine is described. The approaches used have primarily involved polarography at the dropping mercury electrode (dme), cyclic voltammetry at the hanging mercury drop electrode (hmde), and controlled electrode potential electrolysis and coulometry, supplemented by spectrophotometry of electrolyzed solutions.

Previous Investigations. Most pertinent to the present work is a group of recent studies of azines in N,N-dimethylformamide (DMF) and in acetonitrile (AN).[3b,5-11] In apparently the first thorough and systematic study, van der Meer[9] reported a strong dependence between i_d and $E_{1/2}$, and the residual water level of the DMF solvent for eight of the nine diaza aromatics studied. The behavior of most aza aromatics was attributed to a fast ECE mechanism,[12] in which the

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(2) P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967.

(3) (a) J. C. M. Hennlng, J. Chem. Phys., **44**, 2139 (1966); (b) E. W. Stone and A. H. Maki, ibid., **39**, 1635 (1963); (c) R. L. Ward, J. Amer. Chem. Soc., **83**, 3623 (1961).

(4) J. E. O'Reilly and P. J. Elving, ibid., **93**, 1871 (1971).

(5) D. H. Geske and G. R. Padmanabhan, ibid., **87**, 1651 (1965).

(6) K. B. Wiberg and T. P. Lewis, ibid., **92**, 7154 (1970).

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(9) (a) D. van der Meer and D. Feil, Recl. Trav. Chim. Pays-Bas, **87**, 746 (1968); (b) D. van der Meer, ibid., **88**, 1361 (1969); (c) ibid., **89**, 51 (1970).

(10) G. Anthoine, G. Coppens, J. Nasielski, and E. Vander Donckt, Bull. Soc. Chim. Belg., **73**, 65 (1964).

(11) B. J. Tabner and J. R. Yandle, J. Chem. Soc. A, 381 (1968).

(12) An ECE mechanism for a single polarographic wave refers to a process in which an electrochemical step involving electron transfer produces a species which then undergoes a chemical reaction to produce a product unstable at the potential, at which it is formed, and consequently rapidly reduced in a second electrochemical reaction.

Table I. Polarographic Data for the Reduction of Selected Azabenzenes in Nonaqueous Media

Compound	Solvent[c]	$-E_{1/2}$,[a] V	$E_{1/4} - E_{3/4}$, mV	I_d[b]	Column height dependence[k]	Ref
Pyridine	AN	2.66[d]	67	6.07		This work
		2.622[e]	82	6.33		8
	DMF	2.52[f]		4.55		7
		2.62[f]	60	2.4[g]		10
		2.67[h]	64[i]	4.55[i]		6
		2.72[m]				11
Pyridazine	AN	2.203[d]	58	6.50	0.41	This work
(1,2-diazine)		2.120[e]	75	6.35		8
	DMF	2.185[l]	64	3.52		9
		2.13[h]	76[i]	4.79[i]		6
		2.18[m]				11
Pyrimidine	AN	2.337[d]	54	3.39	0.54	This work
(1,3-diazine)		2.340[e]	70	3.58		8
	DMF	2.345[l]	70	2.32		9
		2.30[h]	55[i]	3.01[i]		6
		2.31[m]				11
Pyrazine	AN	2.158[d]	56	5.72	0.50	This work
(1,4-diazine)		2.080[e]	73	6.30		8
	DMF	2.134[l]	64	2.56		9
		2.09[h]	59[i]	3.95[i]		6
		2.13[m]				11
s-Triazine	AN	2.074[d]	50	3.40	0.49	This work
(1,3,5-triazine)	DMF	1.99[h]	53[i]	2.08[i]		6
		2.06[m]		~3		11
as-Triazine	DMF	1.56[h]	60[i]	3.33[i]		6
(1,2,4-triazine)						
s-Tetrazine	DMF	0.81[h]	60[i]	1.87[i]		6
(1,2,4,5-tetrazine)						

[a] Potentials are all reported vs. the aqueous saturated calomel electrode (sce). [b] Diffusion current constant, $I_d = i_d/Cm^{2/3} t^{1/6}$. An I_d magnitude of about 3 in AN and 2 in DMF corresponds to a one-electron faradaic process. [c] AN = acetonitrile; DMF = dimethylformamide. [d] Potential converted to sce by addition of $+0.291$ V to reported $E_{1/2}$ values; background electrolyte 0.1 M tetraethylammonium perchlorate (TEAP). [e] Potential reported in original reference as being vs. aqueous sce; background electrolyte 0.1 M TEAP. [f] Potential converted to sce by adding -0.50 V to reported $E_{1/2}$ values; background electrolyte 0.1 M tetraethylammonium iodide (TEAI). [g] Estimated using the published values for i_d/C, m, and t. [h] Potential converted to sce by addition of -0.516 V to reported $E_{1/2}$ values; background electrolyte 0.1 M TEAI. [i] Slope of the plot of $-E$ (mV) vs. log $[i/(i_d - i)]$. [j] Published value of I_d was multiplied by a factor of 6/7 to convert from maximum to average current values. [k] Column height dependence is the slope of a plot of log i vs. log h_{Hg}; the theoretical slope for a diffusion-controlled wave is 0.50, i.e., the current is proportional to the square root of the mercury column height. [l] Potential converted to sce by addition of -0.005 V to reported $E_{1/2}$ values; background electrolyte 0.1 M TEAP. [m] Potential converted to sce by addition of $+0.042$ to reported $E_{1/2}$ values; background electrolyte 0.1 M tetra-n-butylammonium iodide (TBAI).

electrogenerated radical anion is protonated in a follow-up chemical step and the resulting free radical is immediately reduced in a second electrochemical step.

Usually, however, the primary purpose for studying the electrochemical properties of nitrogen heterocyclic compounds seems to have been to correlate $E_{1/2}$ values with various quantum mechanically calculated parameters. Tabner and Yandle[11] correlated $E_{1/2}$ in DMF for 35 unsubstituted and 19 methyl-substituted nitrogen heterocyclics with Hückel LEMO energies. Millefiori[8] surveyed the polarography and cyclic voltammetry of some 20 azines in AN and obtained distinct regression lines for several classes of compounds between cathodic $E_{1/2}$ and LEMO energy coefficient. The general reduction mechanism for these compounds was assumed or concluded to be similar to that exhibited by aromatic hydrocarbons in aprotic media.[13]

Wiberg and Lewis[6] reported the polarographic behavior of some 17 N-methylazinium ions, azabenzenes, azanaphthalenes, and azabiphenyls in DMF. Surprisingly, it was concluded from cyclic voltammetry that there was no evidence for an ECE reduction mechanism, contrary to earlier conclusions[9,11] which, however, were not cited. In the extended discussion of the "chemical effects" displayed by the anion radicals, ap-

parently as evidenced by the nonappearance of an anodic reoxidation peak, there is only vague indication of the nature of these chemical reactions.

The general criticism which can be made of the reported studies of the azines in nonaqueous media is their failure to explore in sufficient detail the behavior of the compounds involved so as to be able to define the mechanistic and, where feasible, kinetic features of the electrode process in proper detail and perspective.

Results and Discussion

Although all of the five azabenzenes involved in the present study undergo an initial one-electron step in nominally anhydrous acetonitrile, i.e., AN containing only the 0.0005–0.05% H_2O still present[14] in carefully dried solvent as used in electrochemical studies, they differ in respect to the processes seen on normal dme polarography and even rapid scan (up to 150 V/sec) cyclic voltammetry; i.e., pyrimidine and s-triazine undergo one-electron reductions, and pyridine, pyridazine, and pyrazine undergo overall two-electron reductions, which can be shown to be due to ECE processes involving the reaction of the radical anion produced on the initial one-electron transfer with a proton

(13) G. J. Hoijtink, *Advan. Electrochem. Electrochem. Eng.*, 7, 221 (1970); M. E. Peover in "Electroanalytical Chemistry," Vol. 2, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1967, Chapter 1.

(14) V. Gutmann (*Mikrochim. Acta*, 793 (1966)) reports that even the most scrupulously purified acetonitrile still contains at least 0.1–0.5 mM water; consequently, the water concentration will generally be comparable to that of the electroactive species.

source such as the solvent and/or trace amounts of residual water or acidic impurities.

In general, the initial, potential-determining step in the reduction of an azabenzene in AN is a one-electron diffusion-controlled, reversible process. Diffusion control is supported by the dependence of dme current on drop-time (mercury column height; Table I), and by the independence, within experimental error, of $E_{1/2}$ and I_d with concentration. Pyridazine shows the greatest deviation; i.e., the slope of $\log i - \log h_{Hg}$ is 0.41 compared with the 0.50 expected for diffusion control. Pyridine and pyridazine were reported[6] to show a limiting current in DMF proportional to a power of h intermediate between 0.5 and 1.0, supporting partial adsorption control of their reduction. However, adsorption effects are not observed for the reduction of pyridine and pyridazine in AN; other studies on azine reduction in AN[8] and in DMF[9,11] do not mention any adsorption effects.

The wave slopes, $E_{1/4} - E_{3/4}$, for reduction of the diazabenzenes (Table I) are near the 56 mV theoretically expected for a reversible one-electron reduction, even though the diffusion current constants for pyridazine and pyrazine correspond to transfer of about 1.8 and 1.6 electrons, respectively, thus indicating that an initial potential-determining reversible one-electron addition is followed by a fast chemical reaction and further reduction. The larger wave slope for pyridine (67 mV) could reflect either some degree of irreversibility in the electron-transfer process or distortion of the polarographic wave due to the very fast drop-time encountered at very negative potentials. The s-triazine wave slope of 50 mV is sufficiently less than the expected 56 mV to indicate that the wave has probably been affected by fast follow-up reactions.

The $E_{1/2}$ values reported for the reduction of azabenzenes, after conversion to a common reference electrode (Table I), show a remarkable agreement (average deviations generally less than ± 40 mV within a set), especially when one considers the factors which would mitigate against such concordance.[15]

However, it is not the purpose of the present study to correlate polarographic potentials with various molecular orbital calculations, which, as mentioned, has already been done.[6,8,9,11] One point which must be stressed, however, is that extreme care must be taken when correlating polarographic data with molecular orbital calculations, due to the various factors involved,[15] particularly when trying to compare several different molecular orbital methods or in attempts to determine the "best" values for coulomb integrals and bond integrals.

(15) The factors involved include (a) the known effects of fast follow-up reactions on $E_{1/2}$ and of small variations in trace water levels in the solvent on potentials,[4,9] and (b) differences in experimental conditions and equipment among the various investigators, including the use of different reference electrodes which could involve possibly substantial liquid junction potentials.[16] Correction from one reference electrode to another is, at best, a very tenuous procedure. E.g., at least two different values have been reported for the potential of the mercury pool electrode (0.1 M tetraethylammonium iodide as background electrolyte) vs. aqueous sce;[6,7,10,17] some investigators use a modified reference electrode and give little or no indication of its potential.

(16) (a) R. C. Larson, R. T. Iwamoto, and R. N. Adams, Anal. Chim. Acta, 25, 371 (1961); (b) C. K. Mann, in "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1969, pp 63–65; (c) J. F. Coetzee and G. R. Padmanabhan, J. Phys. Chem., 66, 1708 (1962).

(17) P. H. Given, M. E. Peover, and J. Schoen, J. Chem. Soc., 2674 (1958).

Nature of the One-Electron Process. Many aromatic hydrocarbons and conjugated functionalities, e.g., carbonyl groups and carbon–carbon double bonds, undergo an initial one-electron reduction process in aprotic media such as acetonitrile.[18] In acetonitrile,[4] pyrimidine is initially reduced in a one-electron reversible, diffusion-controlled process to produce an unstable radical anion, which is quickly deactivated via two competitive pathways: (1) fast dimerization to form a pyrimidine anionic dimer, and (2) proton abstraction from residual water (rate constant of ca. 7 l./(mol sec), which is rapidly followed by a further one-electron reduction to produce ultimately 3,4-dihydropyrimidine by an ECE process. Addition of acid to pyrimidine solutions in acetonitrile results in the appearance of a new wave at less negative potential, which is attributed to the one-electron reduction of an N-protonated pyrimidine species to produce a free radical which dimerizes very quickly; the latter wave is very similar to the first one-electron wave of pyrimidine in aqueous media.[19]

s-Triazine also gives a one-electron reversible diffusion-controlled wave in acetonitrile. However, the radical anion presumably produced differs markedly from those of the other azabenzenes in terms of its failure to produce a species on addition of water, which would be reducible at the potential of reduction of the parent azabenzene (cf. discussion of Effect of Water Addition).

Since s-triazine did not exhibit an epr spectrum on alkali metal reduction, it was concluded that this compound is not at all reduced by alkali metals.[20] However, since triazine is actually more easily reducible electrochemically than the diazines or pyridine, it is more likely that the radical anion produced on initial reduction disappears due to a very rapid chemical reaction. Since triazine does not undergo the ECE reaction characteristic of other nitrogen heterocycles, but does clearly undergo a one-electron reduction, the subsequent chemical reaction very likely involves a fast reaction of the triazine radical anion with the solvent, analogous to triazine's rapid hydrolysis in aqueous media.[21] Another possibility is dimerization of the radical anion (and the corresponding protonated free radical species) because of the structural similarity of s-triazine to pyrimidine, i.e., the meta positioning of the ring nitrogens.

Nature of the Two-Electron Process. The polarographic behavior in AN of pyridine, pyridazine, and pyrazine, as mentioned, is typical of an overall two-electron reduction process. Since the reported stable radical anion epr spectra of pyrazine in a variety of solvents[3a,b,22] are not consistent with a two-electron reduction and the slopes of the reduction waves, as well as fast scan cyclic voltammetric behavior, are consistent with a one-electron reversible reduction, some chemical reaction must occur after the initial one-

(18) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970.

(19) D. L. Smith and P. J. Elving, J. Amer. Chem. Soc., 84, 2741 (1962); J. E. O'Reilly and P. J. Elving, J. Electroanal. Chem., 21, 169 (1969).

(20) A. Carrington, Quart. Rev. Chem. Soc., 17, 67 (1963).

(21) C. Grundman and A. Kreutzberger, J. Amer. Chem. Soc., 76, 632, 5646 (1954).

(22) (a) A. Carrington and J. dos Santos-Veiga, Mol. Phys., 5, 21 (1962); (b) R. L. Ward, J. Amer. Chem. Soc., 84, 332 (1962).

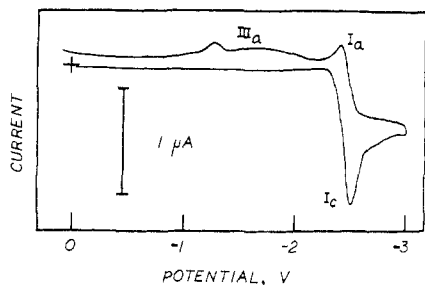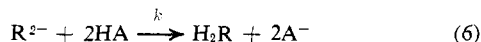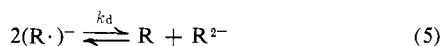Figure 1. Cyclic voltammogram of pyrazine in acetonitrile at the mercury plated disk electrode (mpde):[4] pyrazine concentration, 0.40 mM; scan rate, 400 mV/sec; peaks identified in text.

electron transfer to generate a reducible species, which leads to the large cathodic current observed.

The following ECE mechanism, based on protonation reaction as experienced with aromatic hydrocarbons, has been used to explain the behavior of aza aromatics.[4,9] The radical anion generated in the initial one-electron step abstracts a proton from an available proton source (water, solvent, traces of acids) to form a free radical which is then immediately reduced at the potential of its formation.

$$R + e \rightleftharpoons (R \cdot)^- \tag{1}$$

$$R \cdot^- + HA \xrightarrow{k} RH \cdot + A^- \tag{2}$$

$$RH \cdot + e \rightleftharpoons (RH)^- \tag{3}$$
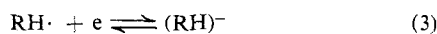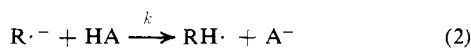
A reaction scheme, which would lead to the nearly two-electron transfer observed and which has apparently not been considered, is one involving disproportionation.

$$R + e \rightleftharpoons (R \cdot)^- \tag{4}$$

$$2(R \cdot)^- \overset{k_d}{\rightleftharpoons} R + R^{2-} \tag{5}$$

$$R^{2-} + 2HA \xrightarrow{k} H_2R + 2A^- \tag{6}$$

The disproportionation reaction scheme[23] is an attractive alternative to the ECE mechanism usually proposed for systems that display some of the same electrochemical behavior as does pyrazine, and is quite possible for pyrazine, since p-quinoidal structures are known and are quite stable. Any dianion generated should be extremely basic, since the dianions of aromatic hydrocarbons are known to abstract protons from solvent and residual water with ease, and would be immediately removed via a reaction such as that of eq 6 (this, of course, could occur in a two- or multistep process).

To help clarify the question as to possible disproportionation or dimerization reactions, the effects of scan rate and concentration on cyclic voltammograms were examined.

Figure 1 presents a typical cyclic voltammogram of pyrazine at moderate scan rate; the behavior on increasing scan rate (Figure 2) is typical of that expected for two separate charge transfers separated by a (moderately) slow chemical reaction. With increasing scan rate, the reduction current for peak Ic decreases because there is insufficient time for the intervening chemical reaction to occur before reoxidation of the electro-
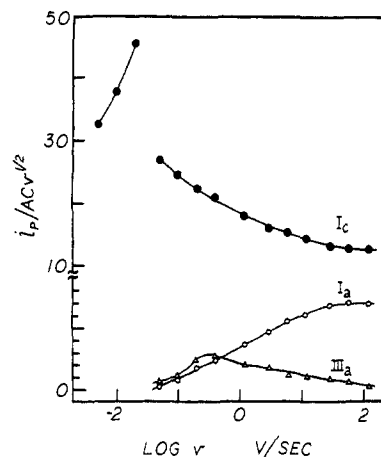

Figure 2. Peak current functions for cyclic voltammetry of pyrazine in acetonitrile. Current magnitudes are measured from the extension of the cathodic and anodic baselines; the current for IIIa was chosen as the height of the largest anodic peak: pyrazine concentration, 1.35 mM; peaks identified in text and in Figure 1.

generated radical anion (cf. Experimental Section for identification of peaks and further details).

Furthermore, if a reaction second order in pyrazine concentration were to occur immediately after the initial one-electron reduction, the anodic current due to reoxidation of the pyrazine radical anion should relatively decrease with increase in concentration.[23,24] The i_a/i_c ratio (Table II) is remarkably constant ($\pm 2\%$)

Table II. Cyclic Voltammetry of Pyrazine in Acetonitrile. Effect of Concentration on the Ratio of Anodic to Cathodic Currents[a]

Pyrazine concn, mM	$-E_p$ for peak I, V		i_a/i_c
	Ic	Ia	
0.076	2.58	2.50	0.72
0.15	2.60	2.49	0.88
0.38	2.63	2.48	0.84
0.76	2.65	2.46	0.86
1.14	2.67	2.45	0.84
1.52	2.71	2.43	0.88
3.04	2.79	2.39	0.86
7.59	2.98	2.28	0.84

[a] Steady-state cycling condition at 54 V/sec scan rate at the hmde. The i_a/i_c ratios were calculated according to the method of Nicholson,[25] which assumes a first-order chemical reaction following initial electron transfer.
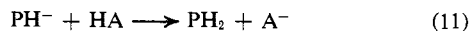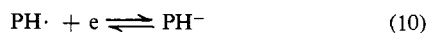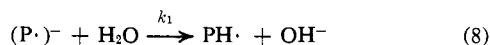
over two orders of concentration magnitude, fulfilling the expectations for a first-order following chemical reaction; moreover, the cyclic voltammetric data for pyrazine do not fit the theoretical expectations[23,24] for dimerization or disproportionation reactions. Thus, disproportionation and dimerization reactions are not important deactivation routes for pyrazine after the initial one-electron transfer (at least at the concentration levels normally employed in polarography), unlike pyrimidine, which undergoes a dimerization reaction following initial electron transfer and does not exhibit a constant i_a/i_c ratio with concentration.[4]

(23) M. L. Olmstead and R. S. Nicholson, Anal. Chem., 41, 862 (1969); M. Mastragostino, L. Nadjo, and J. M. Saveant, Electrochim. Acta, 13, 721 (1968).

(24) M. L. Olmstead, R. G. Hamilton, and R. S. Nicholson, Anal. Chem., 41, 260 (1969).

(25) R. S. Nicholson, ibid., 38, 1406 (1966).

These cyclic voltammetric studies provide positive proof for the ECE reduction mechanism of pyrazine in AN and, when combined with the findings of others,[9] probably also in DMF. We are forced to conclude that the report[6] of there being no evidence for the ECE reduction mechanism for aza aromatics is in error, particularly when it is noted that the reported[6] diffusion current constants for pyridine, pyridazine, and pyrazine, when converted to average current values, average 4.4. It is well accepted[26] that an I_d value of about 2 corresponds to a one-electron reduction in DMF.

1. Measurement of Rate Constants. In order to determine rate constants for the protonation of the pyrazine radical anion and to elucidate the detailed steps in the reduction mechanism, the changes in limiting current and $E_{1/2}$ on addition of water to pyrazine solutions were measured (Figure 3). It is obvious from the high reduction current at even low water concentration that the solvent acetonitrile plays a significant part in the protonation reaction of eq 2. Consequently, the pyrazine reduction is probably best represented by the following sequence of reactions

$$P + e \rightleftharpoons (P\cdot)^- \tag{7}$$

$$(P\cdot)^- + H_2O \xrightarrow{k_1} PH\cdot + OH^- \tag{8}$$

$$(P\cdot)^- + CH_3CN \xrightarrow{k_2} PH\cdot + CH_2CN^- \tag{9}$$

$$PH\cdot + e \rightleftharpoons PH^- \tag{10}$$

$$PH^- + HA \longrightarrow PH_2 + A^- \tag{11}$$

where P represents a pyrazine molecule and HA a proton source such as H_2O or CH_3CN. Reaction 7 is undoubtedly the initial potential-determining step, i.e., a one-electron, diffusion-controlled, reversible reduction. Protonation reactions 8 and 9 are represented as being irreversible, although the back reactions may occur to a limited extent.

The value for the second-order protonation rate constant k_1 for pyrazine, calculated in the manner previously shown,[4,9c,27] is 22 ± 8 l./(mol sec), which is comparable with the value of 5 to 7 l./(mol sec) determined by van der Meer[9c] in DMF solvent; a somewhat higher value would be expected in acetonitrile because of its lesser viscosity.

The value for k_2, the rate constant for protonation of the pyrazine radical anion by the solvent acetonitrile (eq 9), cannot be determined with any degree of certainty since, at the lowest water concentration attainable with the experimental methods employed, the protonation reaction by water is of the same order of magnitude. For an accurate value of $k_2(CH_3CN)$, the water concentration would have to be less than about 0.5 mM which is about the limit of even current vacuum line techniques.[14]

It is clear, however, that acetonitrile is about twice as effective a proton donor as DMF, since, at approximately the same residual water level, the reduction currents for pyrazine in DMF and acetonitrile are about 30 and 60% higher, respectively, than that expected for
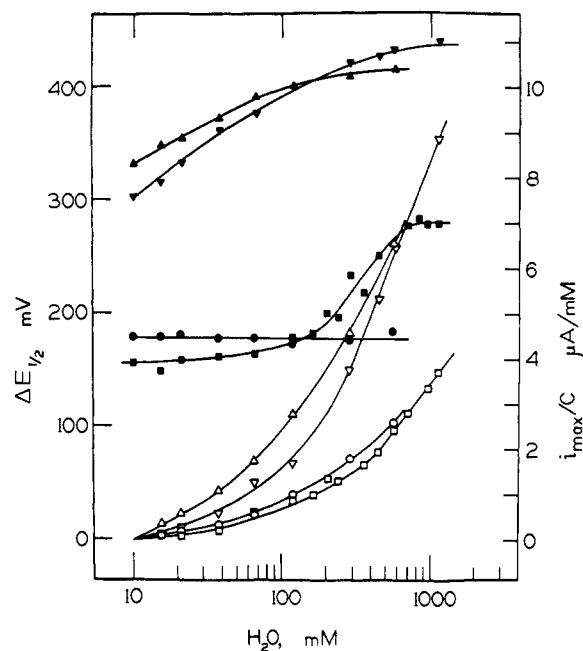

Figure 3. Effect of water on the shift in half-wave potential, $\Delta E_{1/2}$ (open points), and current–concentration ratio, i_{max}/C (solid points), for several azabenzenes: (Δ) 0.92 mM pyridazine; ($\square$) 1.47 mM pyrimidine; ($\triangledown$) 0.68 mM pyrazine; ($\bigcirc$) 0.54 mM s-triazine. Mercury column height, 38 cm.

one-electron reduction. It has been reported[28] that water is a relatively poor proton donor toward aromatic radical anions in DMF due to a degree of structure in water–DMF solutions; on the other hand, water and acetonitrile are not strongly associated, and water is a much better proton donor in this solvent. It has been recently confirmed by other workers[29] that, qualitatively speaking, acetonitrile solvent is a more acidic medium than DMF when roughly equivalent amounts of trace water and tetraethylammonium perchlorate (0.1 M) are present. These observations are in accord with the general view that acetonitrile is a slightly stronger acid, but a much weaker base[30] than DMF.

Others,[31,32] however, have shown that the tetraethylammonium background electrolyte can in some instances function as an effective proton donor, due to the production of roughly equimolar amounts of ethylene and triethylamine on controlled potential electrolysis of several alkyl chlorides and bromines. Since the addition of large amounts of water suppressed ethylene formation[32] in the reduction of norbornane dihalides in DMF–tetraethylammonium bromide (TEAB), and since the reduction of 1-bromo-1-methyl-2,2-diphenylcyclopropane in CD_3CN–TEAB resulted in a hydrocarbon containing 75% deuterium label in the 1 position, it would seem that the primary proton source is the solvent and possibly traces of water. The tetraethylammonium ion can then be attacked by solvent anions such as CH_2CN^-, to produce ethylene and triethylamine.

(26) See, for example, P. H. Given, M. E. Peover, and J. Schoen, J. Chem. Soc., 2674 (1958); P. H. Given, ibid., 2684 (1958); P. H. Given and M. E. Peover, ibid., 385 (1960).

(27) R. S. Nicholson, J. M. Wilson, and M. L. Olmstead, Anal. Chem., 38, 542 (1966).

(28) J. R. Jezorek and H. B. Mark, Jr., J. Phys. Chem., 74, 1627 (1970).

(29) C. P. Andrieux and J. M. Saveant, J. Electroanal. Chem., 33, 453 (1971).

(30) I. M. Kolthoff, M. K. Chantooni, Jr., and H. Smagowski, Anal. Chem., 42, 1622 (1970).

(31) J. L. Webb, C. K. Mann, and H. M. Walborsky, J. Amer. Chem. Soc., 92, 2042 (1970).

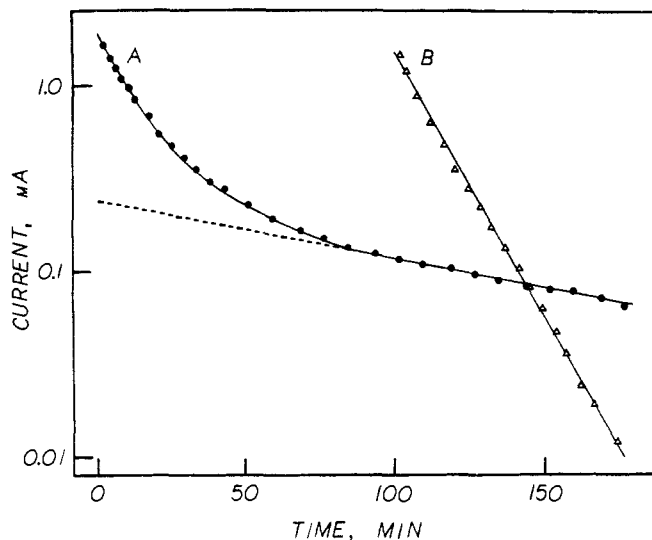(32) A. J. Fry and R. G. Reed, ibid., 93, 553 (1971).

Figure 4. Current *vs.* time curves for the controlled potential electrolysis of pyrazine in acetonitrile: (A) actual current–time curve for electrolysis of 0.265 mM pyrazine at -2.60 V (0.028 mA of residual current has been subtracted from the total current to give the net faradaic current); (B) the current from curve A with the linear portion at long electrolysis time (dashed line) subtracted; the curve has been displaced 100 min along the time axis.

The possibility that the background electrolyte can function as an efficient proton source, however, cannot be excluded.[33] It may well be that particular experimental conditions and the specific nature of the initial electrochemical process are the determinative factors; for example, it is not unlikely that Et_4N^+ may be a good source for hydrogen atom abstraction by electrogenerated noncharged free radicals (as opposed to anionic free radicals or anions) because of the greater ease of homolytically cleaving a C–H bond than an O–H bond.

In general, pyridazine exhibits much the same polarographic and cyclic voltammetric behavior as does pyrazine, and a detailed report of small differences in behavior, some caused simply by the greater reactivity of the pyridazine radical anion, will not be undertaken. Determination of the rate constant, k_1, for the protonation of pyridazine radical anions by water, in a manner analogous to that employed for pyrazine, gives a value of 30 $\pm$ 7 l./(mol sec), in good agreement with the value of 21 l./(mol sec) obtained in DMF.[9c]

Since the reduction current for pyridine is that expected for a two-electron process, the dimerization of pyridine radical anions, which occurs under certain conditions,[3a,c,20,22a] apparently does not occur to an appreciable extent on electroreduction in AN at 25°. In general, the reduction appears to be an ECE process with a very fast intermediate chemical protonation step, to produce an overall two-electron reduction to a dihydro pyridine species.

2. Controlled Potential Electrolysis. Controlled potential electrolysis of pyrazine solutions shows the presence of a fairly rapid overall two-electron process

(33) For further discussions on this subject see, for example: S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955); D. E. G. Austen, P. H. Given, D. J. E. Ingram, and M. E. Peover, *Nature (London)*, **182**, 1784 (1958); D. L. Maricle, *Anal. Chem.*, **35**, 683 (1963); A. K. Hoffman, W. C. Hodgson, D. L. Maricle, and W. H. Jura, *J. Amer. Chem. Soc.*, **86**, 634 (1964); K. V. S. Santhanam and A. J. Bard, *ibid.*, **88**, 2669 (1966); J. S. Mayell and A. J. Bard, *ibid.*, **85**, 421 (1963).

followed by a slower two-electron process (Figure 4); this supports some variation of the following basic mechanism

$$P + n_1e \longrightarrow X \tag{12}$$

$$X \overset{slow}{\longrightarrow} Y \tag{13}$$

$$Y + n_2e \longrightarrow Z \tag{14}$$
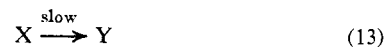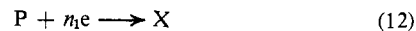
where P stands for pyrazine. The number of electrons, n_1, transferred in the first electrochemical process (eq 12) is two. The latter process probably consists overall of the ECE mechanism outlined in eq 7–11, where the various protonation reactions occur fairly quickly relative to the time scale involved in controlled potential electrolysis. The intermediate X, which is probably the mono- or diprotonated reduced pyrazine species PH^- or PH_2, then undergoes one or more fairly slow chemical reactions to produce a species which participates in the second electron-transfer process involving n_2 electrons. The nature of reaction 14 is uncertain but probably involves reduction of some solvent or background electrolyte decomposition product generated chemically after the initial electron transfer processes; *i.e.*, reaction 13 involves reaction of reduced pyrazine (X) with solvent or background electrolyte to produce Y (*cf.* Experimental Section for further details).

The controlled potential electrolysis of pyrazine in AN shows the behavior characteristic of an ECE mechanism and is an initial overall two-electron process. In contrast, Wiberg and Lewis[6] reported that controlled potential electrolyses of 1 mM solutions of pyrazine and pyridazine in DMF–0.1 M tetraethylammonium iodide were complete after passage of only 0.25 electron per molecule with formation of a black polymeric precipitate. They indicated that this fact supported their proposed *reduction mechanism involving nucleophilic attack on the parent compound by the aza aromatic radical anion.* However, the purity of the DMF used is open to question since it was fractionally distilled "from calcium hydride at atmospheric pressure." It is known[34] that DMF decomposes slightly at its normal boiling point, and calcium hydride is reported to cause substantial decomposition even at room temperature;[34b] the dimethylamine thus generated could interfere under conditions of macroscale electrolysis. The results in DMF, however, could also be due to a specific solvent influence; apparently none of the other electrochemical studies of aza aromatics in DMF have attempted controlled potential electrolysis.[5,7,9–11]

Effect of Water Addition. Addition of controlled amounts of water to AN solutions of the three diazines shifts $E_{1/2}$ to more positive potentials and increases the diffusion current (Figure 3). This behavior supports the ECE mechanism. Figure 3 also indicates the similar electrochemical behavior of pyrazine and pyridazine on water addition, which is in accord with the close similarity in reduction mechanisms.

The addition of water to s-triazine solutions affects the latter's polarographic behavior in a manner quite different from that of the other nitrogen heterocycles studied. With increasing water concentration, $E_{1/2}$ becomes more positive, but the magnitude of the diffu-

(34) (a) Reference 16b, pp 78–79; (b) A. B. Thomas and E. G. Rochow, *J. Amer. Chem. Soc.*, **79**, 1843 (1957).

sion current is unaffected by as much as 1% added water (560 mM). By 1% added water, the reduction of pyrimidine in acetonitrile has clearly become a complete two-electron process due to the ECE process. For pyrazine and pyridazine, where the acetonitrile solvent itself functions as an effective proton donor for the ECE process, the reduction has entirely become a two-electron process by at least 150 and 80 mM added water, respectively. In this respect, the reduction of s-triazine appears similar to that of pyrimidine in DMF,[9a] where the current was unaffected by as much as 1% water although $E_{1/2}$ became 80 mV more positive with increase in water content from 0.08 to 1.35%.

Effect of Acid Addition. Addition of moderately strong acids to AN solutions of the azabenzenes produces a new wave (wave II) at more positive potential than the original azabenzene reduction wave (wave I); wave II grows at the expense of wave I with increasing acid concentration (Figure 5). $E_{1/2}$ for wave II is related both to the base strength of the specific azabenzene and to the strength of the acid used (Table III). A plot of $\Delta E_{1/2}$ ($E_{1/2}$(wave II) $-$ $E_{1/2}$

Table III. Half-Wave Potentials for Acid-Azabenzene Reduction Waves in Acetonitrile[a]

| | | $E_{1/2}$, V | | | | |
| | | Chloroacetic acid added | | | Benzoic acid added | |
Azabenzene	pK_a[b]	Wave I	Wave II	Wave III[c]	Wave II	Wave III[c]
			2.074		2.361	
Pyridine	5.23	2.95	1.867		2.050	
Pyridazine[d]	2.33	2.494	1.464	2.30	1.609	2.15
Pyrimidine	1.30	2.628	1.743		1.898	
Pyrazine	0.6	2.449	1.565	2.25	1.730	2.26
s-Triazine	($\sim$−0.2)[e]	2.365	1.861	2.20	1.952	2.16

[a] $E_{1/2}$ values are vs. Ag | Ag(I) reference electrode; average deviations are generally ±10 mV or less. [b] Aqueous pK_a values from Albert, et al.[35] [c] Wave III shifts to negative potential with increase in acid concentration. [d] Pyridazine also exhibits another acid reduction wave (wave IV); see Figure 5 and text. [e] Aqueous pK_a estimated from substituted compounds; s-triazine itself hydrolyzes rapidly in water.

(wave I)) vs. aqueous[35] pK_a is approximately linear for the diazabenzenes and pyridine. A least-squares analysis of the data results in the following equations for chloroacetic and benzoic acids as the proton source (coefficient of determination[36] ca. 0.8).

Chloroacetic: $\Delta E_{1/2} = 0.86 + 0.045pK_a$ (15)

Benzoic: $\Delta E_{1/2} = 0.71 + 0.040pK_a$ (16)

The points for s-triazine, based on an estimated aqueous pK_a, deviate markedly from these lines, which is not unexpected.

The trend of the $\Delta E_{1/2}$ values is that expected theoretically; as the base strength of the azabenzene increases (larger pK_a), $E_{1/2}$ for wave II is shifted more toward positive potential relative to wave I owing to the increased stability of the azabenzene-proton complex, which would be reflected in decreased electron density in the ring. Similarly, addition of chloroacetic acid,

(35) A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 2240 (1948).
(36) C. Mack, "Essentials of Statistics for Scientists and Technologists," Plenum Press, New York, N. Y., 1967, p 111.
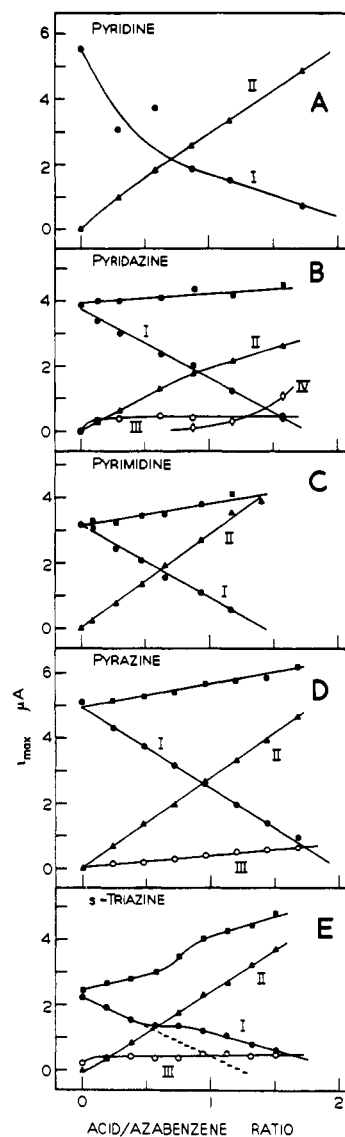
Figure 5. Effect of acid on the polarographic reduction of azabenzenes in acetonitrile: (A) 0.87 mM pyridine; (B) 0.46 mM pyridazine; (C) 1.03 mM pyrimidine; (D) 0.68 mM pyrazine; (E) 0.54 mM s-triazine. Acid added: (A) benzoic acid, (B-E) chloroacetic acid. Identification of waves: (I) normal azabenzene reduction wave; (II) primary azabenzene-acid reduction wave, due to reduction of the protonated azabenzene; (III) small prewave prior to wave I observed on addition of acids to solutions of some azabenzenes; (IV) additional wave produced on addition of acids to pyridazine solutions. The squares give the sum of the currents for the observed waves. Mercury column height, 38 cm. Potentials of the waves are presented in Table III.

which is a stronger acid than benzoic (pK_a's in acetonitrile for chloroacetic and benzoic acids are 9.8 and 12.0, respectively[37]), shifts $E_{1/2}$ for wave II an average of 170 mV more positively.

Wave II is due to reduction of a protonated species, similar to that reported for pyrimidine.[4] However, the original wave I in the case of pyridine, pyrazine, and pyridazine (Figure 5) decreases to nearly zero as the acid/pyrazine ratio approaches 2, indicating that wave II probably involves two electrons and two protons, and not one of each as in the pyrimidine reduction. van der Meer[9b] observed a two-electron reduction wave

(37) G. Charlot and B. Tremillon, "Les Reactions Chimiques dans les Solvants et les Sels Fondus," Gauthier Villars, Paris, 1963, p 377.

for pyrazine in DMF in the presence of excess perchloric acid which was attributed to reduction of the diprotonated species RH_2^{2+}.

s-Triazine, not unexpectedly, exhibits anomalous behavior: wave I initially decreases so as to intersect the zero current axis near an acid/triazine ratio of 1.2, similar to the behavior of pyrimidine, but then shifts so as to intersect at a ratio >2.0.

Wave III, which is seen in polarograms of pyridazine, pyrazine and s-triazine solutions to which acids have been added, is a small wave most probably due to catalytic hydrogen reduction.

Experimental Section

Pyridine was obtained from J. T. Baker; pyridazine, pyrazine, and s-triazine were from Aldrich. Visible and ultraviolet spectra were recorded using 1-cm silica cells, a Beckman Model DB spectrophotometer, and a Photovolt Model 43 strip chart recorder.

Sources and purification of other chemicals, apparatus, and electrochemical procedures have been described.[4] The background electrolyte was 0.1 M tetraethylammonium perchlorate (TEAP).

All potentials, unless otherwise stated, were measured and are reported against a Ag|Ag(I) reference electrode,[4] which has a potential of $+0.291$ V $vs.$ the aqueous sce. Currents at the dme were measured as maximum currents on an undamped polarograph; where necessary, $e.g.$, in the calculation of I_d values, maximum currents were multiplied by a factor of $^6/_7$ to convert to average currents.

The following discussions of specific aspects of the behavior of azabenzenes investigated are intended to amplify and supplement previous statements and the data presented in figure and tables.

Pyridine. Since the pyridine reduction wave in AN ($E_{1/2} = -2.96$ V) occurs adjacent to the background decomposition (about -3.1 V) and the drop-time becomes very rapid and erratic at such negative potential, the pyridine reduction was not studied extensively, even though it is the prototype aza aromatic.

Cyclic voltammograms of pyridine are superficially similar to those produced by most of the azabenzenes studied.[38] On the initial scan, a cathodic peak (Ic) is seen at very negative potential ($E_p = -3.05$ V), which corresponds to the dme wave. On the return scan toward more positive potential, an anodic peak (IIIa) is produced at -1.39 V, which results from the oxidation of a species generated after the initial reduction; on the second and subsequent scans, a small cathodic peak appears at about -1.4 V.

Pyrazine. Cyclic Voltammetry. On scanning a pyrazine solution toward negative potential, a cathodic peak (Ic) is first observed (Figure 1) at about -2.4 V, which corresponds to the dme wave. At slow scan rate, the peak Ic height corresponds to a two-electron or greater reduction; with increasing scan rate, the current decreases and, by 15 V/sec, has leveled off to approximately that expected for a one-electron reduction (Figure 2). However, at very high scan rates, the effects of irreversibility of electron transfer, uncompensated ohmic resistance and slowness of potentiostat response would all be expected to lead to a reduced current magnitude, thus accounting for the continued slight decrease in normalized i_p values. The peak Ic potential becomes more negative with increasing concentration and scan rate.

On the return scan to more positive potential, anodic peak Ia appears, which corresponds to oxidation of the pyrazine radical anion.

At still more positive potential, a series of probably four to six anodic peaks occur between -0.9 and -2.2 V (labeled peaks IIIa), whose potentials and current magnitudes are strongly dependent on such factors as scan rate, concentration, switching potential, and time spent at the negative switching potential. For example, with increasing scan rate, the current magnitude increases to a maximum at about 400 mV/sec, then decreases nearly to zero at very high scan rate, $e.g.$, 80–100 V/sec. Little can be said about the nature of these peaks except that they probably correspond to oxidation of various species generated chemically after the initial 1e transfer. At moderate scan rates, these products are electrochemically oxidized before they can diffuse away from the electrode surface or possibly decompose via secondary reactions; at very high scan

rates, however, there is insufficient time for the generating chemical reaction to occur so that little anodic current is produced.

On the second and subsequent cycles at a given scan rate, no new cathodic peaks are observed prior to the main pyrazine reduction peak, although there is some change in the shape and magnitude of peaks IIIa. On recycling within the potential range of peaks IIIa, no new cathodic peaks appear and the current magnitude for these peaks greatly diminishes, approaching zero. These facts indicate that the processes producing peaks IIIa are totally irreversible, form highly unstable products, or both.

Cyclic voltammograms of pyrazine solutions containing more than nominal (10 mM) water concentrations exhibit effects which can be explained by the increased protonation of electrogenerated pyrazine anion. With 30 mM water added, the peak Ic current is increased at all scan rates by about 30% over that for nominally dry AN solutions. Peak Ia, attributed to reoxidation of the pyrazine radical anions, disappears at scan rates <1 V/sec; rather high scan rates are needed to observe it. Peaks IIIa, attributed to irreversible oxidation of various protonated products of reduced pyrazine, increase in magnitude by a factor of 3 to 6 at low scan rates and become more numerous.

Pyrazine. Controlled Potential Electrolysis. Pyrazine does not exhibit the simple, clean one-electron reduction characteristic of pyrimidine on controlled potential electrolysis in acetonitrile. The log current–time plot (Figure 4A) displays the two linear segments characteristic of certain ECE mechanisms.[39] Moreover, the electrolysis current does not decay to the background current level even after 4 to 8 hr, probably indicating that a very slow chemical reaction to form a reducible species occurs after the primary electrode reaction is complete; this behavior complicates the evaluation of the total number of coulombs passed during an electrolysis.

The total number of electrons involved in the pyrazine reduction, obtained by integration of the area under the current–time curves, is generally between 4.0 and 4.5 per molecule; the value depends somewhat on the magnitude of the residual current correction.

If the current, obtained by extrapolating the linear log current–time plot at long electrolysis times back to $t = 0$, is subtracted from the total current flowing (Figure 4A), a second linear log i $vs.$ t plot is produced (Figure 4B) which corresponds to the current for the primary electrochemical process. The number of electrons involved in the latter can be calculated by (a) integration of the area under the current–time curve for the secondary and slower electrochemical process and subtraction from the total coulombs passed, or (b) assuming the theoretical relation $i_t = i_0 \exp(-\rho t)$ to be true for each linear segment and mathematical integration to obtain the coulombs passed. The n thus calculated is about 2.2, regardless of whether the residual current deducted is that after preelectrolysis of the background electrolyte or the somewhat larger current still flowing after prolonged electrolysis of pyrazine solutions; although the total n value is affected, n for the first electrochemical process is constant and only n for the secondary or slower process is affected.

The mass transfer constant, ρ, calculated from the slope of the current–time plot for the initial two-electron pyrazine reduction is close to that for the linear pyrimidine reduction mentioned under similar conditions, indicating that the first pyrazine process is mass-transport limited: for pyrimidine, $\rho = 1.5 \times 10^{-3}$ sec^{-1}; for pyrazine, $\rho_1 = 1.0 \times 10^{-3}$ and $\rho_2 = 1.6 \times 10^{-4}$ sec^{-1}.

Pyrazine. Spectrophotometric Studies. On controlled potential electrolysis, pyrazine solutions turn a bright yellow, which slowly fades on prolonged electrolysis. The final electrolyzed solutions are generally light yellow. In the latter solutions, the characteristic fine structured ultraviolet absorption spectrum of pyrazine in AN (λ_{max} at 254 nm (ϵ 5620), 261 (ϵ 6130), 267 (ϵ 3990), 314 (ϵ 720)) is replaced by a single fairly broad maximum at 254 nm which tails off rather gradually into the visible region, giving the light yellow color. For electrolyzed 0.5 and 1.0 mM pyrazine solutions, this maximum had molar absorptivities of 32,000 and 25,000, respectively, based on the original pyrazine concentration.

Electrolyzed pyrimidine solutions also exhibit an absorbance maximum at about 250 nm (ϵ 5400). In studies of carbon–halogen bond fission for several aliphatic, aromatic, and aza aromatic halides in AN,[40] electrolysis at a potential corresponding to cleavage of the carbon–halogen bond results in solutions exhibiting absorb-

(38) See Figure 3A in ref 4 or Figure 1 in ref 8.

(39) R. I. Gelb and L. Meites, $J. Phys. Chem.$, **68**, 630, 2599 (1964).
(40) J. E. O'Reilly and P. J. Elving, unpublished results.

ance maxima in the 250–254-nm region (ϵ 3000–14,000). Since quick distillation of the electrolyzed solutions through a short column resulted in a distillate which had absorption spectra corresponding to AN solutions of the nonhalogenated aromatic compound, i.e., no large absorbance at 250 nm, the product giving rise to this large absorbance is most probably some solvent or background electrolyte decomposition product, possibly polymeric in nature. Other data[40] indicate that at least two different solvent decomposition processes are operant in electrolyzed AN solutions, the exact natures of which are unclear at present.

Pyridazine. Dc Polarography. In an effort to see if the rate of the intervening protonation reaction could be slowed down appreciably, polarography was performed at −23° (CCl_4–solid CO_2 freezing mixture[41]).

The temperature coefficient for diffusion-controlled current in aqueous media is generally[42] about 1 to 2%°. For kinetic currents, in which the height of the wave is partly or wholly determined by the rate of a chemical reaction that produces the electroactive substance, the temperature coefficient is usually larger because the temperature coefficients for most chemical reactions are considerably larger than those for diffusion.

The temperature coefficient for the simple one-electron diffusion-controlled reduction of rubidium(I) to the amalgam used to establish a standard for purely diffusion-controlled processes in acetonitrile, was 0.7% over the temperature interval of −23 to 25°. Over the same temperature interval, the temperature coefficient for the pyridazine reduction is 0.8%, indicating that the activation

energy for protonation of the pyridazine radical anion is probably quite low.

s-Triazine. Cyclic Voltammetry. On scanning a s-triazine solution toward negative potential, the first peak observed is a cathodic peak (Ic) at about −2.4 V that corresponds to the dme wave seen (Table I). Its normalized peak current function closely corresponds to that expected for a one-electron reduction and is relatively independent of concentration and scan rate up to about 30 V/sec.

On the return scan toward more positive potential and on the second and subsequent cycles, a series of anodic and cathodic peaks appear in the region of −0.5 to −1.3 V. With increase in scan rate (up to 100 V/sec), some of these peaks become quite large, e.g., up to about five times the magnitude of peak Ic. The number of these peaks and their variation in potential and current magnitude with factors such as scan rate and concentration, prevent formulation of hypotheses regarding the chemical and electrochemical reactions producing them, except to say that they result from the oxidation and reduction of various short-lived intermediates which arise from fragmentation of the triazine ring and decomposition of the solvent/background electrolyte.

Cyclic voltammograms of s-triazine solutions containing benzoic acid also show a peak at about −2.1 V, corresponding to wave II for reduction of the protonated s-triazine species. A peak corresponding to wave III is seen only on the first scan. The magnitude of the anodic and cathodic peaks in the −0.5 to −1.3 V region is greatly diminished by benzoic acid addition. The set of anodic–cathodic peaks at −0.3 to −0.5 V, which are generally observed[4] on the reduction of acids in AN (peaks Va and Vc), are also observed.

(41) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, New York, N. Y., 1966.
(42) L. Meites, "Polarographic Techniques," 2nd ed, Interscience, New York, N. Y., 1965, p 139.