also indicate that the double hydrogen bond is stronger than two separate single hydrogen bonds. It is tempting to postulate that the mutarotation in the micellar core involves hydrogen bonding both between the dodecylammonium ion and the heterocyclic oxygen atom and between the 1-hydroxyl group and the carboxylate ion of the surfactant, thereby facilitating ring opening (eq 7). The large upfield shift observed for the ammonium protons as a function of tetramethylglucose concentration supports such a postulate. A functional catalytic mechanism of this type is consistent with the observed kinetic results if the ring opening reaction is rate determining and the surfactant *via* hydrogen bonding facilitates this step. The probability of double hydrogen bonding with the surfactant is predictably far greater in the core of the micellar phase than in the bulk solvent.

Acknowledgments. The authors express their thanks to Dr. P. Rony for a sample of 2,3,4,6-tetramethyl-α-D-glucose which was used in preliminary experiments and for helpful discussions. This work was supported, in part, by the U. S. Atomic Energy Commission. E. J. F. is a Research Career Development Awardee of the National Institutes of Health.

Electrochemical Reduction of Pyrazine in Aqueous Media[1]

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Abstract: The reactions associated with the reduction of pyrazine (I) in aqueous media are highly dependent upon solution pH. In 1 *M* $HClO_4$ three polarographic waves are observed. The first two waves are successive reversible one-electron steps yielding the radical cation of 1,4-dihydropyrazine (II) and 1,4-dihydropyrazine (III), respectively. Controlled potential coulometry is characterized by a mass transport process with *n* values of 2.00 ± 0.01. A rapid and reversible reaction between I and III yielding II is observed at pH <2. The third wave is a catalytic hydrogen wave with a species derived from III serving as the catalyst. The decomposition of III is first order and is acid–base catalyzed. Above pH 2 a single diffusion-controlled two-electron reduction is observed. The reversibility of this wave decreases with increasing pH. Coulometric *n* values are dependent upon stirring rate, concentration of I, and pH. Functional group tests indicate that the decomposition of III involves ring opening at an N–C site yielding $H_2NCH{=}CHNHCH_2CHO$ (IV), which subsequently polymerizes. In phosphate buffers a polymer of $-CH{=}NCH_2-$ precipitates. Spectral evidence indicates that the carbonyl group of IV or a polymer of IV is reduced during exhaustive electrolysis. Uv data indicate the above mechanism is valid up to pH 7.

Of the three unsubstituted isomeric aromatic diazines, pyrimidine is the most thoroughly studied, probably because the purine, adenine, and other derivatives are of great importance in the biological sciences. Derivatives of pyrazine, some of which occur naturally, have found use as pharmaceuticals.[2] Pyridazine derivatives, none of which occur naturally, are used as antifungicidal agents for stored food stuffs. Other derivatives have found some use as pharmaceuticals.[3]

The redox behavior of these compounds has received modest attention. Elving and coworkers[4] have devoted considerable effort to the electrochemical reduction of pyrimidine and its derivatives. Detailed mechanisms have been presented for several compounds.[5] Fragmentary results for the reduction of pyrazine have been reported,[6-10] but these studies *in toto* are incomplete and contradictory. The work reported herein is a detailed investigation of the electrochemical reduction of pyrazine in well-buffered aqueous media.

Experimental Section

Pyrazine (I), Puriss grade from Aldrich Chemicals (Milwaukee, Wis.), was used without further purification. Uv and ir spectra confirmed its purity and identity. All other chemicals were reagent grade quality and used without further purification. Perchloric acid and phosphate buffers (C_{PO_4} = 0.37 *M*) were used to control pH. $NaClO_4$ was used to maintain the ionic strength of the final test solutions at 1.0.

Polarographic data were obtained with a stabilized Heath (Benton Harbor, Mich.) Polarographic System. For detailed wave-shape and half-wave potential studies the potential axis was expanded such that the cell potential could be read directly from the polarogram to the nearest 0.5 mV.

For cyclic voltammetric and chronoamperometric studies an all-solid-state operational amplifier potentiostat designed similar to the one reported by Smith, *et al.*,[11] was used. An X–Y recorder or

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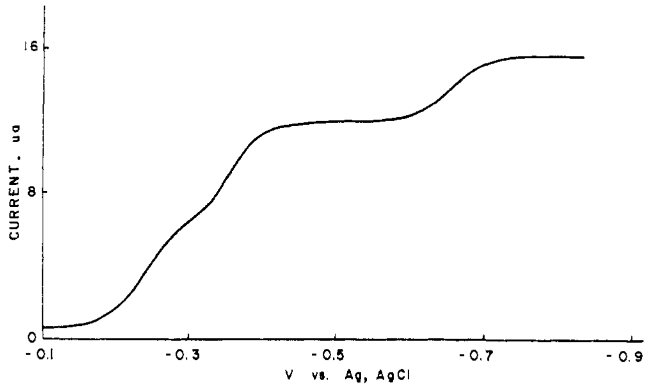

Figure 1. Polarogram of1.3 mM pyrazine in 1 M $HClO_4$.

storage oscilloscope served as the read-out devices. The input signal was obtained from a Wavetek (San Diego, Calif.) Model 112 signal generator.

The potentiostat described by Harrar and Behrin[12] was employed for bulk electrolysis experiments. Current–time curves were integrated digitally through use of a voltage-to-frequency converter and an electronic counter.

Voltammetric and coulometric cells were designed to minimize total and uncompensated cell resistance and optimize the performance of the cell–potentiostat system. All potentials are referred to a Ag|AgCl reference electrode saturated with NaCl. The temperature was maintained at 25.0 ± 0.1°.

Uv, visible, and esr spectra data were obtained *via* conventional techniques applicable to aqueous media. The electron spectra were obtained with the apparatus described by Jack and Hercules.[13]

Results and Discussion

Dc Polarography. Below pH 2 three distinct waves are observed in the reduction of pyrazine. The first two waves have been previously reported,[9] while the third has not. Figure 1 shows a typical polarogram of pyrazine in 1 M $HClO_4$.

Limiting currents for all three waves are directly proportional to pyrazine concentration. The heights of the first two waves are independent of acid concentration, indicating that these waves are not due to the reduction of a protonated and unprotonated form of pyrazine. The height of the third wave increases linearly with increasing acid concentration. The limiting current for the sum of the first two waves is proportional to the square root of the mercury pressure, indicating a diffusion-limited process. However, the limiting current of the third wave is independent of the mercury pressure.

Accurate half-wave potentials for the first two waves are not obtainable even in 1 M H_2SO_4 because they are not completely resolved. Further discussion of these two waves will be presented in the section on cyclic voltammetric results.

Half-wave potentials for the third wave are dependent upon solution pH and pyrazine concentration, and slightly dependent upon drop time. The shift in the half-wave potential of the third wave with increasing pH is given by

$$-E_{1/2} = 0.048\text{pH} + 0.619 \qquad (\text{pH} < 2)$$

The wave shifts negatively about 7 mV for each tenfold increase in pyrazine concentration. Decreasing the drop time shifts $E_{1/2}$ to more negative values.

The limiting current, i_l, at constant pH is directly proportional to pyrazine concentration, while at constant pyrazine concentration the limiting current decreases with increasing pH up to pH 2, above which the wave is no longer observable.

Plots of E *vs.* log $((i_l - i)/i)$ are nonlinear. The wave becomes considerably elongated with increasing pH and pyrazine concentration as shown by the $E_{3/4} - E_{1/4}$ data given in Table I.

Table I. Dependence of Wave Shape upon Pyrazine Concentration and Solution pH for the Third Polarographic Wave

pH	[Pyrazine], mM	$E_{3/4} - E_{1/4}$, mV
0.01	0.129	−37.2
0.01	0.65	−41.6
0.01	1.29	−43.2
0.01	2.07	−46.5
0.01	4.13	−54.3
0.35	1.29	−44.8
0.60	1.29	−71.5
0.86	1.29	−82.5
1.01	1.29	−94.0

The results thus far suggest that the third wave involves a catalytic hydrogen reduction. According to Mairanovskii,[14] there are two types of catalytic hydrogen waves. An absolute requirement for both types is the presence of a Brønsted base. In surface catalytic waves the protonated species is more easily reduced in the adsorbed state than in the solution state. This process is characterized by a limiting current that approaches a maximum value as the concentration of the base increases. This maximum current corresponds to the maximum amount of protonated base that can be adsorbed on the electrode surface. Plots of the limiting current *vs.* concentration of catalyst (base) have the same general shape as Langmuir adsorption isotherms.

The other type, known as volume catalytic waves, does not involve adsorption in the reduction pathway. One might expect the pyrazine reduction product to fall into this latter category because similar nitrogen analogs yield volume catalytic waves.[14,15]

In an effort to distinguish between the two possible mechanisms, drop time studies were initiated from 0.0 to 1.0 V in order to determine if any species are absorbed at the electrode surface. The electrocapillary curves in the presence and in the absence of pyrazine are indistinguishable, suggesting that adsorption is not significant. Therefore, it is rather unlikely that the reduction involves an adsorbed species as required for a surface catalytic hydrogen wave. Furthermore, the observed limiting current does not approach a limiting value with increasing pyrazine concentration as required for a surface-catalyzed wave. The current–time curves of individual drops are normal in all respects.

Surface active agents were added to the polarographic cell in order to further substantitate the absence of adsorption in the reduction mechanism of the

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third wave. These agents should be selectively adsorbed on the electrode surface and hopefully block any adsorption due to the electroactive species. Thus, if the mechanism involves the reduction of the adsorbed electroactive species, one should expect a drastic decrease in the limiting current upon the addition of the surfactant. A cationic surfactant (methyl red in acidic solution) was used because it is preferentially adsorbed at potentials negative of the electrocapillary maximum (*i.e.*, the region where the third wave is observed). A nonionic detergent (Triton X-100) was also used because it is absorbed over a wide range of potentials. Concentrations up to 0.004% were used with no apparent effect on the limiting current. Therefore, the third wave is not a surface catalytic hydrogen wave.

With the assumption of reversible charge transfer, Mairanovskii derived current–voltage relationships for volume catalytic waves,[14] thus establishing criteria for the experimental verification of this type of wave. Reversible volume catalytic waves are asymmetric and plots of E *vs.* log $((i_l - i)/i^{2/3})$ should be linear with a slope of $59/n$ mV at 25°. Half-wave potentials should shift negatively 40 mV with an increase of 1 pH unit and shift positively by 20 mV per tenfold increase of catalyst concentration. To determine if the third wave followed this behavior, an exhaustive wave shape study was completed.

The shape of the third wave was ascertained through use of an expanded potential scale. Pyrazine solutions in 1 M $HClO_4$ whose concentration varied from 0.129 to 4.13 mM were studied. The general shape of the third wave changes very little but, as the data of Table I show, the slope of the wave decreases with increasing pyrazine concentration. Furthermore, the dependence of the half-wave potential upon pyrazine concentration is not in accord with theory.

When the concentration of pyrazine is held constant and the acid concentration varies from 0.1 to 1.0 M $HClO_4$, the wave shape changes. Two distinct slopes appear in the rising portion of the wave in solutions from 0.1 to 0.5 M $HClO_4$. The first portion of the curve appears reversible, while the second portion is very irreversible. As the acid concentration decreases, the reversible segment becomes a smaller fraction of of the total rising portion of the polarogram. Plots of E *vs.* log $((i_l - i)/i^{2/3})$ at acid concentrations greater than 0.5 M are nonlinear.

The failure of the observed wave to conform to the shape predicted by Mairanovskii does not mean that this wave is not a volume catalytic hydrogen wave primarily because Mairanovskii's derivation is based upon two assumptions. The first assumption is that the charge transfer is reversible, which apparently is not true in the present case. The second assumption is that the reduction proceeds as follows

$$B + H^+ \rightleftharpoons BH^+ \qquad (1)$$

$$BH^+ + e^- \longrightarrow BH \qquad (2)$$

$$2BH \longrightarrow 2B + H_2 \qquad (3)$$

where reaction 1 is the rate-determining step. At very low catalyst concentration reaction 3 may become the rate-determining step, but this should not be true at the concentrations used in this study. As will be shown later, B is formed by a first-order decomposition of 1,4-dihydropyrazine. Thus, the experimental system differs from the theoretical model considered by Mairanovskii, and the criteria he developed cannot be quantitatively compared with the experimental data. Therefore, this wave will be classified as a volume catalytic hydrogen wave based upon the qualitative agreement with similar systems.[14,15]

Over the pH range 2–7 only a single wave is observed which shifts to more negative potentials and becomes progressively elongated with increasing pH. The pH dependence of this wave is given by

$$-E_{1/2} = 0.086\text{pH} + 0.266 \quad (2 < \text{pH} < 7)$$

which is in accord with the 90 mV prediction for a three-proton, two-electron reduction. The magnitude of the diffusion current observed in this pH region is equal to the sum of the limiting currents for the first two waves in 1 M $HClO_4$; thus, the wave observed in this media should involve the same number of electrons as the sum of the first and second waves in 1 M $HClO_4$. The dependence of the limiting current upon mercury pressure indicates that the reduction is diffusion controlled.

To determine if adsorption was present, drop time studies in the presence and in the absence of the electroactive material were carried out. Since the electrocapillary curve obtained for the solution with the pyrazine is identical with the curve obtained without the pyrazine, adsorption is not indicated.

Above pH 7 only a single polarographic wave is observed which becomes very drawn out and ill defined. The diffusion current decreases substantially from that observed below pH 7. Variations of the limiting current with mercury pressure indicates a diffusion-controlled reduction. Electrocapillary curves failed to reveal any adsorption.

Controlled Potential Coulometry. Electrolysis on the plateau of the second wave ($E_{\text{applied}} = -0.550$ V) in solutions below pH 2 yield an n value of 2.00 ± 0.01 which is independent of concentration over the range 0.65–20 mM pyrazine. Plots of log (i) *vs.* time are linear, indicating a mass transfer controlled reduction. Since the two polarographic waves are of approximately equal height, each wave, therefore, involves a single electron in the reduction pathway.

During the electrolysis of 1.3 mM pyrazine the initially colorless solution turns a violet-blue and then colorless at completion of the electrolysis. In more concentrated solutions, the final color is a light amber which darkens with time. This appearance and subsequent disappearance of the violet-blue color suggest the involvement of a moderately long-lived intermediate in the reduction pathway.

When an electroylsis is carried out on the rising portion or as close as possible to the plateau of the first polarographic wave ($E_{\text{applied}} = -0.26$ V), the solution also turns violet-blue but the color persists after completion of the electrolysis. Coulometric n value data are not particularly useful at this potential because the two polarographic waves are not well resolved.

Esr spectra were obtained from the violet-blue solution prepared at both electrolysis potentials. In each case the spectrum and the hyperfine splitting constants

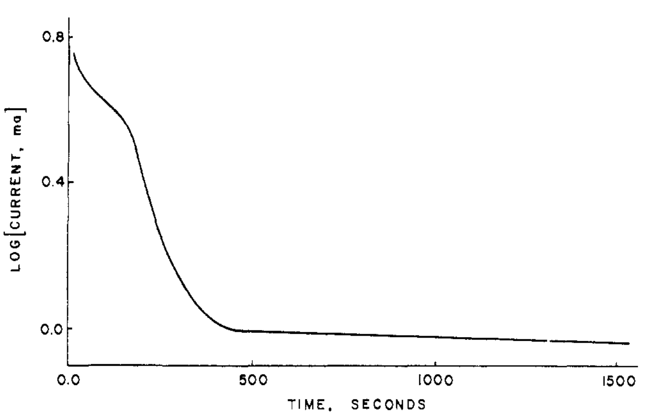

Figure 2. Log (*i*) *vs.* time plot of 0.64 m*M* pyrazine electrolyzed at −0.800 V in 1 *M* $HClO_4$.

were identical with that found in the literature for the 1,4-dihydropyrazine radical cation.[16]

Based upon this evidence, the product of the first reduction step at pH's below 2 is 1,4-dihydropyrazine radical cation (II). The second reduction step involves the reduction of this radical intermediate to a protonated form of 1,4-dihydropyrazine (III). The product of the second electrochemical reaction, III, reacts with pyrazine in a homogeneous chemical reaction producing 2 mol of II.

When a 0.65 m*M* pyrazine solution is electrolyzed at −0.800 V (*i.e.*, on the plateau of the third polarographic wave), the current decays in an irregular manner and then attains a nonzero steady-state value. Figure 2 shows this behavior in terms of a log (*i*) *vs.* time plot. The observation of a steady-state current is characteristic of a cyclic regeneration of the electroactive species.[17,18] As the concentration of pyrazine is increased, the steady-state current decreases. For solutions more concentrated than 5 m*M* pyrazine, the electrolysis current decreases in a regular manner to zero; however, the log (*i*) *vs.* time plots are concave upward.

If a very dilute solution of pyrazine is exhaustively electrolyzed at −0.550 V and then the potential rapidly shifted to −0.800 V, further electrolysis is observed. The current from this process is essentially time independent and its magnitude is dependent upon the time interval between the completion of electrolysis at −0.550 V and the initiation of electroylsis at −0.800 V. The behavior is shown in Figure 3.

Before proposing a mechanism for the coulometric behavior and comparing it with the polarographic data, it is important to remember that the two sets of data may not be complementary owing to the differences in the amount of product generated as well as differences in time scale. However, in this particular study there seems to be a great deal of correlation. Both techniques indicate that the electrochemical processes for the first two polarographic waves are diffusion controlled, the process responsible for the third waves is not diffusion controlled, and solutions containing less than 5 m*M* pyrazine when electrolyzed at −0.800 V indicate the presence of a cyclic regeneration reaction.

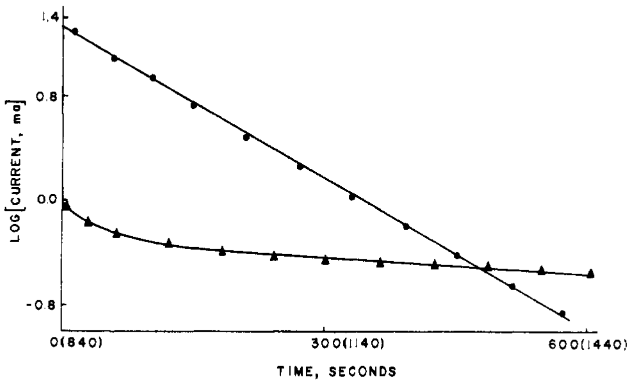

Figure 3. Log (*i*) *vs.* time for a sequential electrolysis of 1.29 m*M* pyrazine in 1 *M* $HClO_4$: (●) $E_{\text{applied}} = -0.550$ V, (▲) $E_{\text{applied}} = -0.800$ V. Units in parentheses correspond to electrolysis at −0.800 V and denote total elapsed time for the experiment.

To explain the inverse relationship between initial pyrazine concentration and steady-state current one can postulate that the reactants responsible for the cyclic regeneration reaction can undergo a competing homogeneous reaction which yields an electroinactive species. To test this postulate, exhaustive electrolysis was carried out on the plateau of the second polarographic wave. Successive polarograms for the third wave were then obtained directly in the coulometric cell, and it was found that the limiting current decreased with increasing time. These data are summarized in Table II. Assuming that the limiting current is proportional to the bulk concentration of the reactant for the third wave, one should be able to determine the order of this reaction by plotting various functions of *i vs.* time. At concentrations above 3 m*M* plots of 1/*i vs.* time are linear indicating that the disappearance of the reactant is second order. The rate constant is 0.5 M^{-1} $\sec^{-1}$ in 1 *M* $HClO_4$.

Table II. Polarographic Decomposition Rate Study for Third Reduction in 1 *M* $HClO_4$

Time, min[a]	$E_{1/2}$, V	i_1, μA
	8.26 m*M* Pyrazine	
5.5	−0.649	2.45
11.25	−0.648	1.32
17.5	−0.650	0.802
23.0	−0.647	0.628
	4.13 m*M* Pyrazine	
8.5	−0.645	0.789
20.5	−0.650	0.368
37.5	−0.667	0.302

[a] $t = 0$ at completion of electrolysis at $E_{\text{applied}} = -0.550$ V.

Above pH 2 the *n* values for solutions of 1–3 m*M* pyrazine electrolyzed on the plateau of the single polarographic wave are not reproducible, varying between 2 and 3. These electrolyses take an inordinate length of time to complete. Stirring rate studies of 4.13 m*M* pyrazine buffered at pH 4.80 indicate that the *n* value is directly proportional to stirring rate. The log (*i*) *vs.* time plots for the maximum stirring rate have a slight upward bow, while those at the slowest stirring rate are essentially linear.

In an effort to ascertain information about the structure of the final electrolysis product a uv spectrum was

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obtained from a sample prepared by exhaustive electrolysis of 6.5 mM pyrazine in 1 M $HClO_4$ on the plateau of the second polarographic wave. A weak broad band is observed at 320 nm along with the indication of a very strong band below 200 nm. The intensity of the 320 nm band decreases slowly with time. Exposure of the solution to the atmosphere accelerates the rate of disappearance of this band, while band below 200 nm is unaffected.

If electrolysis is carried out on the plateau of the third wave with a solution identical with the one above, an identical uv spectrum is obtained. Since these spectra are identical, one can assume that the absorption is not due to the product of either the second or third electrochemical reaction; rather, it is due to the product formed by the second-order homogeneous decomposition reaction. The possibility that the 320-nm band is due to a small amount of the strongly absorbing 1,4-dihydropyrazine radical cation can be discounted based upon Moorehead and Britton's data.[9] Absorption due to unreacted pyrazine can also be discounted because it does not show any bands above 300 nm in aqueous media.[19]

The ultraviolet spectrum of a freshly electrolyzed solution of 6 mM pyrazine at pH 2 contains a weak broad band at 320 nm and the intense shoulder below 200 nm. The rate of decrease in the intensity of this 320-nm band upon exposure to the atmosphere is considerably greater than that observed in 1 M $HClO_4$.

Functional group analyses were carried out on approximately 0.1 M pyrazine solutions in 1 M $HClO_4$ during different stages of electrolysis. The tests for carbonyl and primary aliphatic amine were initiated to determine if these groups were present as a result of hydrolylic ring opening. The Tollens silver mirror test suggested the presence of a carbonyl group during the middle and early stages of electrolysis. A blank consisting of a portion of unelectrolyzed pyrazine in 1 M $HClO_4$ failed to give a positive test. Identical portions of electrolysis solutions were tested for primary aliphatic amine utilizing nickel chloride and 5-nitrosalicylaldehyde.[20] An immediate copious precipitate was observed, indicating the presence of this group.

Electrolyzed solutions of 0.1–0.2 M pyrazine at pH 3 turned amber shortly after initiation of the reduction and a flocculent precipitate formed. When the precipitate was separated from the mother liquor, it was found to be insoluble in carbon tetrachloride, benzene, chloroform, cyclohexane, and dioxane. After several washings with distilled water and drying under vacuum at 25° the material was found to melt with decomposition at 263–265°.

A KBr pellet was prepared from the dried material, and the resulting ir spectrum is shown in Figure 4. The spectrum is characterized by a broad ammonium band at 3350 and 2950 cm^{-1}. These bands can primarily be attributed to the NH stretching frequency of a protonated amine. Absorptions for the NH_3^+ group in the solid state have been reported in the range 3350–3150 cm^{-1} and sometimes appear as a multiplicity of bands. If a NH_3^+ group is present, a moderately strong band near 1600 cm^{-1} should be present, corresponding to the asymmetric deformation, and a band for the symmetric mode near 1300 cm^{-1}. The bands at 1605 and 1280 cm^{-1} appear to satisfy these predictions.

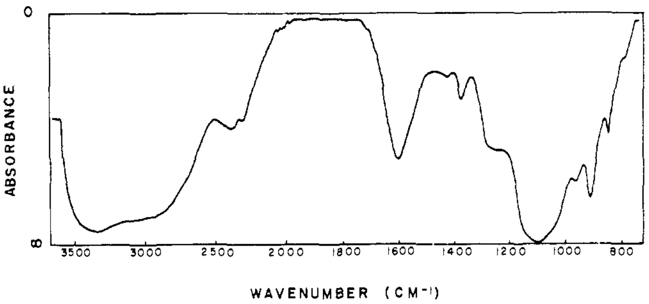

Figure 4. Ir spectrum of precipitate isolated from electrolysis solution of 30.0 mM pyrazine at pH 3.01, KBr mull.

The band at 1605 cm^{-1} could be due to C=N vibration of imines, 1640–1633 cm^{-1},[21] as well as the NH_3^+ asymmetric deformation, because the shape of the band suggests the presence of two nearly coincident bands.

The strong broad band at 1090 cm^{-1}, along with the weaker band at 975 cm^{-1}, is attributed to the presence of inorganic phosphate. Miller and Wilkins[22] suggested that the first band is shifted to somewhat higher frequencies with the hydrogen phosphates. Bellamy[21] reported that for the hydrogen phosphates the OH stretching frequency is not found in the normal region but instead appears as a broad shallow absorption in the range 2700–2560 cm^{-1}. This could be responsible for the tailing nature of the broad band at 3000 cm^{-1}.

Based on the evidence of the ir spectra it appears that the compound of interest is an aliphatic ammonium hydrogen phosphate salt possibly containing an imine group. Little else can be said about its structure with any degree of certainty.

Electron spectroscopy was employed to verify the presence of the elements and functional groups proposed from the ir spectrum. Two coalesced peaks with a 2:1 peak height ratio were observed in the nitrogen 1s spectrum. The peak of greatest intensity had a binding energy of 399.0 eV. Nitrogen groups yielding a photoelectron peak at this binding energy include azide, cyanide, amide, hydrazine, and imine.[23] Considering the nature of the product of the last electron transfer, its possible chemistry, and the observed infrared spectrum, the first four groups are highly improbable. Thus, it appears that the photoelectron peak at 399.0 eV is due to an imine.

The lesser nitrogen peak had a binding energy of 400.9 eV which is in the region associated with charged nitrogen groups. A protonated aliphatic amine would be the only group consistent with the infrared spectrum. Peak height ratios suggest there is twice as much imine nitrogen as ammonium nitrogen.

The carbon 1s spectrum consisted of a single broad asymmetric photoelectron peak having a binding energy of 285.0 eV. Probable contamination by hydrocarbon pump oil prevented any meaningful correlation between carbon and nitrogen peak height ratios.[24]

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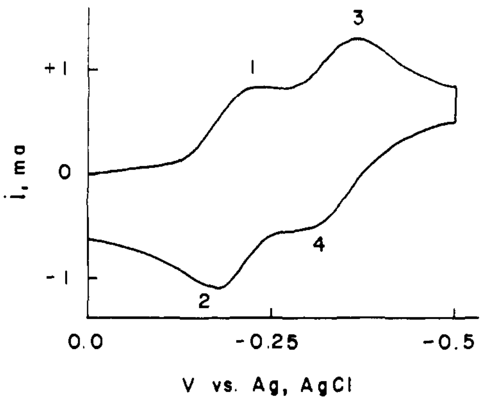

Figure 5. Cyclic voltammogram of 1.3 m*M* pyrazine in 1 *M* $HClO_4$, scan rate = 50.0 V/sec.

A single, broad, low-intensity peak was observed in the phosphorus 2p photoelectron spectrum. Its binding energy of 133.1 eV was in the range one would expect for phosphate phosphorus. Thus, it appears that the ESCA results substantiate the original infrared interpretation.

Because the solid compound melted with decomposition, which is typical for organic amine salts, several attempts to obtain a usable mass spectrum were unsuccessful.

Cyclic Voltammetry. In Figure 5 a typical cyclic voltammogram of pyrazine in 1 *M* $HClO_4$ is shown. At pH values less than 1.5 two distinct reduction steps are observed. In the pH range 1.5–2.5 these two waves coalesce into the single wave which is observed at pH values greater than 2.5. All of the reduction waves shift to more negative potentials with increasing pH. The anodic peak currents for all the waves decrease with decreasing scan rate. In the very acidic solutions i_{p_2} is always greater than i_{p_4}.

Since the current is proportional to $n^{3/2}$,[25] the number of electrons involved in a particular reduction or oxidation has a considerable effect upon peak shape. If the number of electrons in two electrochemical steps are the same, then the shapes of the two peaks are identical. In order to test this hypothesis, a peak-shape study was carried out in 1 *M* $HClO_4$. The shape of the combined peaks as obtained in the usual manner. To determine the shape of the second peak, a linearly increasing cathodic potential was applied until it reached a value approximately 30 mV past the first peak potential and then held constant. In this manner the concentration of pyrazine at the electrode surface was reduced to zero and the current decayed in the normal $t^{-1/2}$ manner.[26] Subtraction of this current from the total current yields the current due to the second peak. Individual peak currents are almost identical, and the shape of the two peaks are the same. $E_p - E_{p/2}$ for each peak is 58 mV which is very close to the theoretical value of 56.5 mV for a one-electron reversible reduction. Since the coulometric data indicated that the overall reduction involved 2.0 electrons, each individual step must involve a single electron.

Table III. Peak Potential Dependence upon Scan Rate[a]

pH	Scan rate, V/sec	V *vs.* Ag|AgCl E_{p1}	E_{p2}	E_{p3}	E_{p4}
−0.04	0.05	−0.230	−0.164	−0.347	−0.292
	0.10	−0.232	−0.167	−0.342	−0.295
	10.0	−0.230	−0.176	−0.353	−0.297
	100.0	−0.228	−0.176	−0.360	−0.300
0.96	0.05	−0.334	−0.267	−0.428	−0.360
	10.0	−0.338	−0.270	−0.432	−0.362
1.41	0.05	−0.375	−0.300	−0.442	−0.378
	10.0	−0.375	−0.308	−0.446	−0.383
2.94	0.05	−0.545	−0.496		
	1.0	−0.550	−0.494		
	100.0	−0.578	−0.470		
4.70	0.05	−0.700	−0.641		
	1.0	−0.707	−0.651		
	100.0	−0.823	−0.614		
5.25	0.05	−0.736	−0.678		
	1.0	−0.748	−0.682		
	100.0	−0.880	−0.649		
6.98	0.05	−0.916	−0.776		
	1.0	−0.965	−0.773		
	100.0	−1.006	−0.738		

[a] 1.29 m*M* pyrazine.

The dependence of peak potential upon scan rate was investigated over a range of 2000 in scan rate. Table III summarizes these data as a function of pH. At pH's <1.5, the first reduction peak potential, E_{p_1}, is independent of scan rate while the corresponding oxidation peak potential, E_{p_2}, shifts negatively with scan rate. The second reduction peak, E_{p_3}, shifts slightly negative with increasing scan rate. This behavior is usually associated with slow charge-transfer kinetics or a succeeding chemical reaction. If this shift is due to a kinetically controlled electron transfer, the separation between the reduction and oxidation peak potentials increases with increasing scan rate. Data from Table III show that $E_{p_3} - E_{p_4}$ remains close to the theoretical value of 57 mV for a reversible one-electron reduction.[25] This result indicates that the product of the second electron transfer undergoes a chemical reaction subsequent to the charge-transfer reaction.

At pH values between 2.5 and 5.5 the differences between reduction and oxidation peak potentials are close to the theoretical values at the slower scan rates. As the scan rate increases, potential shifts due to slow electron transfer are observed. At pH 6.98 and higher the electron transfer reaction appears irreversible at all scan rates.

The peak potentials are independent of pyrazine concentration when potential shifts due to uncompensated cell resistance are accounted for.

E_{p_1} is linear with pH over the range 0–1.4 and shifts to more negative potentials, 104 mV/pH, which is reasonably close to the value expected for a two-proton, one-electron reversible reduction. This result is in agreement with the coulometric and esr data which indicated that 1,4-dihydropyrazine radical cation is the product of the first electron transfer.

A least-squares fit of E_{p_3} *vs.* pH yields a reasonably straight line with a slope of 60 mV/pH. This is in good agreement with theory for a one-proton, one-electron reversible reduction. These results indicate that the product of the second electron transfer is a protonated form of 1,4-dihydropyrazine.

In the pH range 3–5, the wave corresponds to a reversible two-electron reduction, at least at the slower scan rates. A shift in peak potential of 90 mV/pH

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[25] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
[26] D. S. Polcyn and I. Shain, *ibid.*, **38**, 370 (1966).

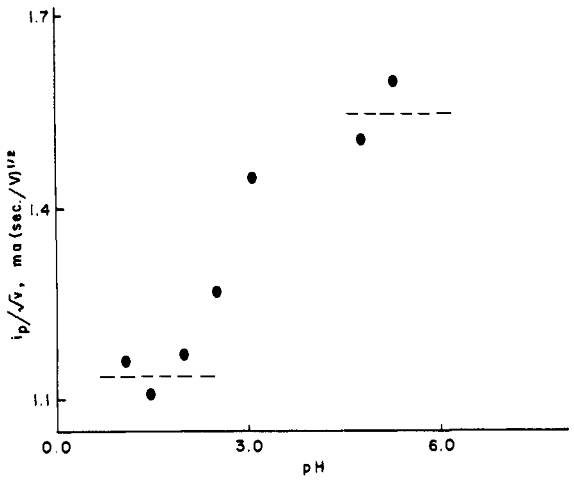

Figure 6. Cathodic peak current function *vs.* pH, scan rate = 0.05 V/sec, 1.3 mM pyrazine. Dotted lines correspond to average values at low and high pH, respectively.

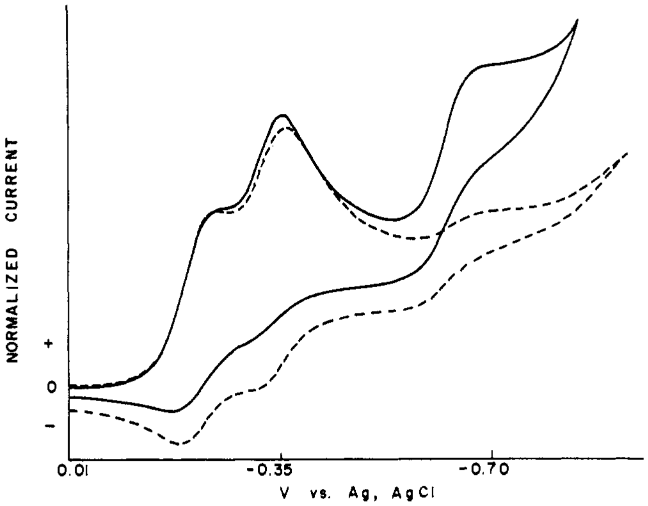

Figure 7. Cyclic voltammogram of pyrazine at slow scan rates, 1 mM pyrazine in 1 M HClO$_4$: (——) 0.02 V/sec, (- - - -) 0.20 V/sec.

was obtained which is in good agreement with the expected value for a two-electron, three-proton reversible reduction, and agrees with the polarographic results under the same conditions.

Table IV summarizes peak current data as a function of scan rate, v, for 1.3 mM pyrazine in 1 M HClO$_4$. Except for the most rapid scan rate i_{p1}/i_{p3} is constant. Both $i_{p1}/\sqrt{v}$ and $i_{p3}/\sqrt{v}$ are independent of scan rate. One would normally expect $i_{p3}/\sqrt{v}$ to decrease somewhat with increasing scan rate when the product of the electron transfer undergoes a succeeding homogeneous chemical reaction. However, such effects are quite small and are probably hidden in the uncertainty of the measurements. Peak potentials are a more sensitive parameter for observing effects due to succeeding chemical reactions. Since i_{p1}/i_{p3} is independent of scan rate, the presence of a slow intervening chemical reaction is not possible.

Table IV. Anodic and Cathodic Peak Current Dependence upon Scan Rate in 1 M HClO$_4$[a]

Scan rate, V/sec	i_{p1}/i_{p3}	i_{p1}/i_{p2}	i_{p3}/i_{p4}	i_{p2}/i_{p4}
0.05	1.07	3.1	5.8	2.0
0.01	1.03	3.0	5.8	1.8
1.0	1.05	1.7	2.3	1.4
10.0	0.98	1.6	1.9	1.2
100	0.85	1.3	2.1	1.5

Scan rate, V/sec	μA (sec/V)$^{1/2}$			
	$i_{p1}/\sqrt{v}$	$i_{p2}/\sqrt{v}$	$i_{p3}/\sqrt{v}$	$i_{p4}/\sqrt{v}$
0.05	75.4	24.1	69.6	12.0
0.01	73.3	24.1	71.5	13.4
1.0	69.0	39.6	65.2	28.3
10.0	69.8	42.8	71.4	36.6
100	67.0	51.0	79.0	34.0

[a] 1.29 mM pyrazine.

Examination of cathodic to anodic and anodic to anodic peak current ratios provides considerable information about the details of this system. The anodic peak current ratio, i_{p2}/i_{p4}, decreases with increasing scan rate up to a scan rate of 0.5 V/sec and then remains constant at 1.4. The ratio i_{p3}/i_{p4} behaves in a similar manner but attains a constant value of 2.3. This result should not be observed for an uncomplicated stepwise process.[26] If one assumes that 1,4-dihydropyrazine is involved in a reaction which yields an electroinactive substance, the increase of i_{p_2} over i_{p_5} would be explained.

As previously mentioned, peak currents are directly proportional to $n^{3/2}$ where n is the number of electrons involved in a particular reaction. In solutions below pH 2.0 the total peak current ($i_{p_1} + i_{p_2}$) is proportional to $n_1^{3/2} + n_2^{3/2}$ with $n_1 = n_2 = 1$. Above pH 3.0 pyrazine is reduced directly to 1,4-dihydropyrazine and the peak is characteristic of a two-electron process, with total peak current proportional to $2^{3/2}$. Figure 6 illustrates the increase in peak current as a function of pH for solutions containing 1.3 mM pyrazine. Taking an average of 1.15 mA/(V/sec)$^{1/2}$ for $i_{p_t}/\sqrt{v}$ in very acidic media where the waves are separated and 1.56 mA/(V/sec)$^{1/2}$ for $i_{p_t}/\sqrt{v}$ at pH values 3–5, a ratio of 1.36 is obtained. Considering that the theoretical ratio for peak currents of a single two-electron reaction to successive one-electron reductions is 1.41, the observed value is in excellent agreement with theory[25] and indicates that as the pH increases the reduction pathway changes from successive one-electron steps to a single two-electron process.

In very acid media three waves were observed in the polarographic study. However, when a cyclic voltammogram is recorded using identical solutions, only the first two peaks are observed when the scan rate is greater than 50 mV/sec. At a scan rate of 25 mV/sec, a very small peak at more negative potentials is observed. Decreasing the scan rate even further results in an increase in the cathodic and anodic currents for this third wave. Figure 7 illustrates this behavior with 1.3 mM pyrazine in 1 M HClO$_4$. Although the shapes of the waves are somewhat distorted by solvent discharge, the third cathodic peak appears sigmoidal, which is characteristic of a cyclic regeneration reaction.[25] Peak currents are quite uncertain because of the solvent discharge. It should be noted that the position of the wave appeared to be independent of scan rate over this limited range, and the cathodic and anodic peaks were separated by approximately 0.16 V.

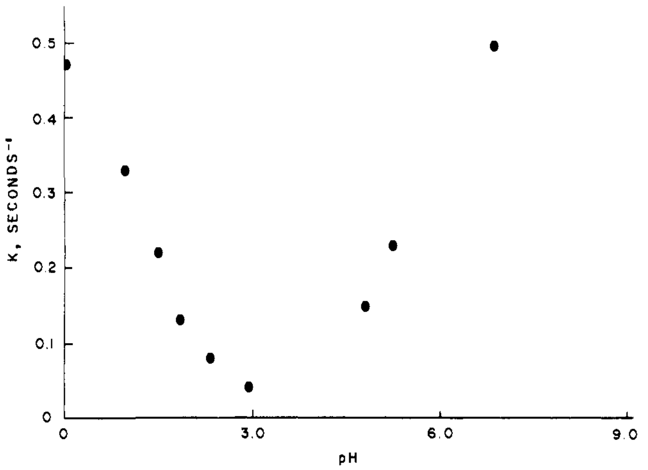

Figure 8. Decomposition rate dependence upon pH, 1.29 m*M* pyrazine.

Since the third peak is not present at the faster scan rates, this indicates that 1,4-dihydropyrazine is electroinactive. Rather, it must undergo a slow reaction that produces the reactant for this wave. This same reaction produces the changes in anodic currents of waves 2 and 4 (Figure 5 and Table IV) at the slower scan rates. Furthermore, this latter substance is the catalyst producing the volume catalytic hydrogen wave observed in polarographic and coulometric experiments.

Chronoamperometry. Double step chronoamperometry was used to study the kinetics of the disappearance of 1,4-dihydropyrazine and to check the stability of the radical cation intermediate. The theory behind this technique was developed for planar geometry by Schwarz and Shain with the assumption that the chemical reaction is first order and that the product of the reaction is electrochemically inactive.[27]

To determine the stability of the radical cation the potential was set at the foot of the first cyclic voltammetric wave and approximately 30 mV past the first peak potential in a solution of 1.3 m*M* pyrazine in 1 *M* $HClO_4$. By computing anodic to cathodic current ratios at various normalized time intervals and employing working curves given by Schwarz and Shain,[27] the kinetic parameter, $k\tau$, characterizing the decomposition reaction can be evaluated. A value of zero was obtained indicating that the radical cation is stable, at least on the time scale used in these experiments.

Similar experiments were performed to evaluate the kinetics of the succeeding reaction. The potential was set at the foot of the first reduction wave and a few millivolts past the second reduction peak. Under these conditions pyrazine is reduced directly to 1,4-dihydropyrazine and then oxidized to pyrazine. If the measured rate constant is to have any validity, any intermediate products such as the radical cation must not undergo any coupled chemical reactions that would reduce or increase the expected current ratios. The previous experiment indicated that the radical cation is stable. There is, however, a possible problem due to the proposed reaction between 1,4-dihydropyrazine and pyrazine forming the radical cation. Ideally, the decrease in the anodic current should correspond solely to the decomposition of 1,4-dihydropyrazine. Based upon the cyclic voltammetric study, the reaction between pyrazine and 1,4-dihydropyrazine is rapid. Furthermore, for every mole of 1,4-dihydropyrazine that is consumed in the reaction with pyrazine, 2 mol of the radical cation is formed. Therefore, the decrease in anodic current corresponds to the amount of 1,4-dihydropyrazine that is converted to an electroinactive substance.

The anodic to cathodic current ratios are summarized in Table V for a solution of 1.3 m*M* pyrazine in 1 *M* $HClO_4$. Several different switching times were used in an effort to obtain a switching time, τ, as close to the half-life of the coupled reaction as possible. A value of 1.0 sec was used in the 1 *M* $HClO_4$ study. At this switching time a shift to higher $k\tau$ values at longer times is observed. This is due to the spherical nature of the drop which gives larger currents than a planar electrode of the same area. The average $k\tau$ value yields a first-order rate constant of 0.47 sec^{-1}. At 20.7 m*M* pyrazine in 1 *M* $HClO_4$ a rate constant of 0.32 sec^{-1} was obtained. The constancy of k with changes in pyrazine concentration indicates that the reaction is first order.

Table V. Data for Decomposition of 1,4-Dihydropyrazine in 1 *M* $HClO_4$

$(t - \tau)/\tau$	$-i_a/i_c$	$k\tau$
0.1	0.552	0.34
0.2	0.399	0.48
0.3	0.332	0.47
0.4	0.282	0.48
0.5	0.247	0.46
0.6	0.217	0.46

Similar experiments were carried out at various pH's. Figure 8 contains a summary of the observed rate constants for the disappearance of 1,4-dihydropyrazine as a function of pH. The rate constant decreases with increasing pH, reaching a minimum at approximately pH 3, then increases with increasing pH. This behavior is typical of an acid–base catalyzed reaction.

Generally, the first-order rate constants for an acid–base catalyzed reaction can be given by

$$k_{obsd} = k_O + k_{H^+}[H^+] + k_{OH^-}[OH^-] \qquad (4)$$

where contributions from other acids and bases in solution are neglected.[28] Values for the various rate constants were obtained *via* a least-squares fit of eq 4 to the data of Figure 8. At the 95% confidence limit k_O, k_{H^+}, and k_{OH^-} are 0.16 ± 0.08, 0.32 ± 0.23, and 4.6 ± 3.2 × 10^6, respectively. The effect of various Brønsted acids and bases was not tested; thus, the question whether the decomposition of 1,4-dihydropyrazine is specific or general acid–base catalyzed cannot be answered.

Conclusions

The cumulative data indicate that the reduction in very acid media proceeds *via* two steps.

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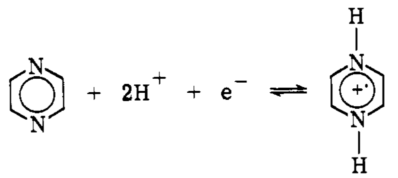
(27) W. M. Schwarz and I. Shain, *J. Phys. Chem.*, **69**, 30 (1965).

(28) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960.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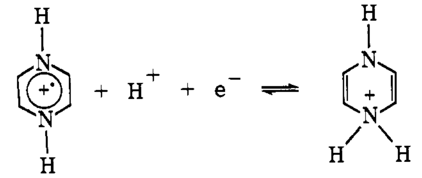
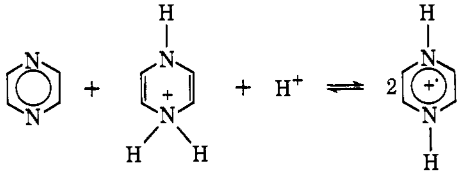

(6)

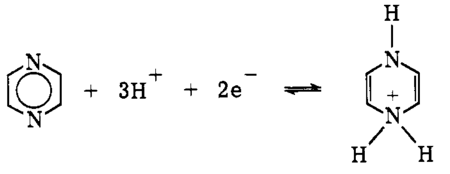
Coulometric evidence shows that the total reduction involves two electrons and is mass transport controlled. Polarographic diffusion currents for each step are independent of pH and are of equal height; thus, each step involves a single electron. Cyclic voltammetric peak shape studies confirmed this result. Scan rate studies indicate that reaction 5 is reversible. Peak potentials for reaction 6 shift in a manner typical of a reversible charge transfer reaction followed by a slow succeeding chemical reaction.

Since a free radical is present during massive electrolysis at applied potentials corresponding to the addition of one electron (reaction 5) and the addition of two electrons (reaction 5 plus reaction 6), a homogeneous reaction between pyrazine and protonated 1,4-dihydropyrazine must occur.


(7)

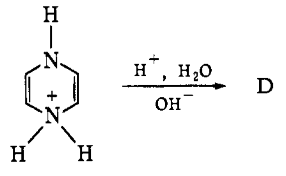
Scan rate data indicate that reaction 7 is rapid. Based upon the difference in peak potentials for reactions 5 and 6 (Table III), the equilibrium constant for reaction 7 in 1 M $HClO_4$ is 10^2.

When the pH is greater than 2.5 pyrazine is reduced in a single step to protonated 1,4-dihydropyrazine.


(8)

At these pH's reaction 7 no longer occurs. Reaction 8 is reversible only at the slower scan rates investigated.

The decrease in peak current for the oxidation of protonated 1,4-dihydropyrazine with decreasing scan rate indicates that it undergoes a chemical reaction which yields an electroinactive substance. Double-step chronoamperometric measurements indicate that this latter reaction is first-order with respect to pyrazine and shows evidence of being acid–base catalyzed.


(9)

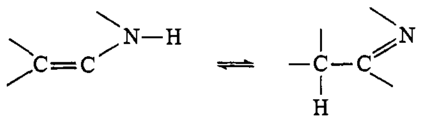
A previously unreported third reduction is observed in the polarographic experiments at high acidities. Variations in limiting currents with mercury pressure indicate the wave to be nondiffusional controlled and that the half-wave potentials are dependent upon drop time. The latter result is usually characteristic of a kinetically controlled charge-transfer reaction. Limiting currents as well as wave shape are dependent upon acid concentration. The independence of the limiting current upon surfactant concentration and the linear dependence of the limiting current upon pyrazine concentration suggest that this wave is due to a volume catalytic hydrogen wave. The presence of this wave only at the slowest scan rates in the cyclic voltammetric experiments indicates that substance D of reaction 9 is the catalyst.

In order to explain the disappearance of the catalytic hydrogen wave with increasing pyrazine concentration, substance D must be involved in a reaction which yields an electroinactive substance, E. Based upon the decrease of the third polarographic wave with time, after exhaustive reduction of pyrazine to protonated 1,4-dihydropyrazine, the conversion of D to E was found to be second-order with respect to D. The presence of this reaction is substantiated by the fact that identical uv spectra are obtained regardless of whether controlled potential electrolysis is carried out on the plateau of the second or third polarographic wave and irrespective of the presence or absence of the steady-state coulometric current.

It was not possible to obtain information about the structure of substance D directly. Thus, its structure must be postulated on the basis of indirect chemical and spectral information. Since D is the product of the decomposition reaction of 1,4-dihydropyrazine, one might expect it to be related to the structure of its precursor. 1,4-Dihydropyrazine probably exists as a protonated and unprotonated form in rapid equilibria. Since 1,4-dihydropyrazine is a reasonably strong base, it probably exists primarily as the protonated form in the pH range studied.

The functional group test for primary amine was positive, suggesting that the C–N bond has broken, thus opening the ring. The test for carbonyl was also positive, suggesting that this group is also present during electrolysis. The uv spectrum of incompletely electrolyzed pyrazine supports the presence of a carbonyl group.

To explain this behavior let us consider the structure of 1,4-dihydropyrazine as consisting of two enamine groups. Enamines are generally unstable if hydrogen is attached to the nitrogen atom and rearranged to form the corresponding imine.[29,30]


(10)

The rearrangement corresponds to a rapid proton shift tautomerization with the imine predominating.[31] Thus, 1,4-dihydropyrazine undergoes a tautomeric

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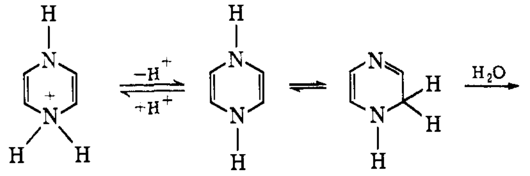
(29) J. D. Roberts and M. C. Casserio, "Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964.

(30) B. Witkop, *J. Amer. Chem. Soc.*, 78, 2873 (1956).

(31) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, Structures," McGraw-Hill, New York, N. Y., 1968.

proton shift to form the corresponding imine which is rapidly hydrolyzed, breaking the ring, resulting in the formation of an aliphatic amino carbonyl compound, IV.



$NH_2CH{=}CHNHCH_2CHO$ (11)

IV

Since the elimination of water is used to effect ring closure in similar systems (*i.e.*, Friedlander quinoline synthesis;[32] in fact, substituted dihydropyrazines are prepared *via* cyclic condensation of α-amino ketones),[33] it would not seem unreasonable that a partial reverse of this condensation could occur under appropriate conditions. Furthermore this hydrolysis would be consistent with the observed functional group analysis.

Substance IV can either polymerize, eliminating a mole of water, or, since there is still another enamine group present, it can also tautomerize to form the corresponding imine which would be hydrolyzed to form 2 mol of acetalamine. Thus substance D probably corresponds to acetalamine or IV.

α-Primary amino carbonyl compounds, of which acetalamine is a member, can rarely be isolated because of their strong tendency to condense.[34] Thus, the second-order decomposition is probably due to the polymerization of acetalamine or IV. Substance E is probably a mixture of oligomers derived from condensation of IV.

The protonated amine polymer is stabilized by precipitation as the dihydrogen phosphate salt. In the absence of phosphate no precipitate is formed and the solution continues to darken, suggesting the formation of higher oligomers. The protonated dihydrogen phosphate trimer of acetalamine would give a 2:1 ratio of imine to protonated amine nitrogen. It is quite likely that the precipitate contains a mixture of compounds representing different degrees of polymerization.

Infrared analysis failed to indicate the presence of a carbonyl group in the precipitate. A possible explanation for this is to postulate that the carbonyl group is reduced electrolytically to the corresponding alcohol. The infrared spectrum does not give any clear evidence but does not rule out that possibility. The reduction of the carbonyl group would explain why the observed *n* values are always greater than two when electrolysis is carried out at the more negative potentials. The formation of the hydroxyl group would eliminate further polymerization.

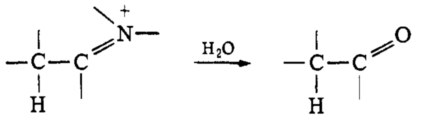
The rate of decomposition of protonated 1,4-dihydropyrazine was found to be catalyzed mainly by base and to a much smaller extent by acid. Ultraviolet spectral information suggested that the products are the same in each case. Reaction 11 involves nucleophilic attack of a water molecule on the >C=N- site of 1,4-dihydropyrazine and is base catalyzed.

To explain the acid catalysis a mechanism involving electrophilic attack is proposed. Consider the resonance structures for enamines

V

VI

Electrophilic attack on the β carbon by H^+ would yield



(12)

VII

VII which would then hydrolyze to IV. Since the product of reaction 12 is the same as that of reaction 11, it will undergo the same type of following chemical reactions, *i.e.*, tautomerization, hydrolysis, and polymerization. Since VI represents a small contribution to the resonance forms of enamines, the acid catalysis would not be particularly large.

Uv data and all electrochemical data suggest that the proposed mechanism is valid up to pH 7.

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(32) A. R. Katritzky and J. M. Lagowski, "The Principles of Heterocyclic Chemistry," Academic Press, New York, N. Y., 1968, p 23.

(33) Reference 32, p 84.

(34) J. J. Krems and P. E. Spoerri, *Chem. Rev.*, 40, 279 (1947).