

POLAROGRAPHIC BEHAVIOR OF A SERIES
OF SUBSTITUTED HYDRAZINES

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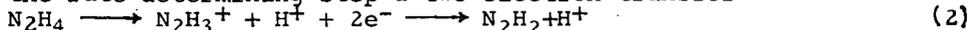
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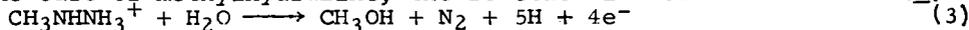
The oxidation of hydrazine and its organic derivatives is of importance in a number of areas. One may cite the use of hydrazines as propellents, as oxygen scavengers, in fuel cells, or as electrode depolarizers, to name just a few applications. In almost all cases, the oxidation path of the hydrazine controls its utility. Chemically, hydrazine oxidation proceeds through a diimide or hydrazyl radical to form nitrogen, or nitrogen and ammonia, or ammonia and hydrazoic acid, depending on the conditions of reaction (1). Electrochemical studies of hydrazine (4, 2) and of methylhydrazine (5) have shown that an overall four-electron reaction of the following sort takes place:



with the rate-determining step a two-electron transfer



In the case of methylhydrazine, the reaction in acid solution is (5)



The work presently reported was undertaken to elucidate some of the reasons for the apparent differences in stability of organic hydrazines. In particular, the electrochemical behavior of a series of monosubstituted hydrazines was studied. In order to minimize ambiguities due to the catalytic effects of noble metals (1), such as those found with platinum electrodes (2, 5), a normal dropping mercury electrode was utilized in strongly basic solution. This experimental arrangement produces well defined, reversible anodic waves easily interpreted (4).

EXPERIMENTAL

Chemicals - Monomethylhydrazine (MMH), 1,1-dimethylhydrazine (UDMH), 1,2-dimethyl hydrazine (SDMH), 1,2-diisobutylhydrazine (DiBH), *n*-hexylhydrazine (nHH) and acetic hydrazide (AcX) (Olin Mathieson Chemical Corp.) were distilled under reduced pressure and assayed by an iodometric titration (7). Hydrazine sulfate and diacetyl hydrazine (DACX) (Olin Mathieson Chemical Corp.) were recrystallized from water. Ethyl hydrazine acetate hydrochloride (EtH) and *n*-propyl hydrazine oxalate (PrH) (K and K Laboratories) were used without further purification, but assay indicated the purity to be 84%. Phenyl hydrazine hydrochloride (Eastman White Label) also was used without further purification. All other chemicals were reagent grade.

APPARATUS - A Sargent Model XXI polarograph was used in conjunction with a thermostated H-cell (25.0 ± 0.1°C.) containing a saturated mercurous sulfate reference electrode (6). The mercurous sulfate reference was used to permit the application of more positive voltages. The capillary used had a constant of 1.98 mg^{2/3} second^{1/6} at 25 cm. of Hg.

PROCEDURE - Stock solutions of the hydrazines were prepared immediately before use and degassed with nitrogen pre-saturated with a portion of the stock solution. Background electrolyte solutions (0.1M sodium hydroxide-0.005% gelatin) were deoxygenated for 10

minutes in the H-cell and the requisite volume of hydrazine stock solution added. The mixture was mixed thoroughly and the polarogram run immediately. All polarograms were run using a span of 0.5 volts with the initial and final voltages measured accurately with a Rubicon Portable Precision potentiometer. $E_{1/2}$ and i_d values were obtained graphically using the average of the recorder traces.

RESULTS AND DISCUSSION

In order to maintain conditions as constant as possible, all the hydrazine samples were run at ca. 0.5 mM concentration. The effect of any concentration dependency of the half-wave potentials thus would be minimized. Table I lists the polarographic values obtained for a variety of substituted hydrazines in 0.1M NaOH, vs. a mercurous sulfate electrode.

The results for the monosubstituted alkyl hydrazines is of particular interest. In general, as the carbon skeleton is lengthened, the half-wave potential is shifted to more negative voltages. A plot of $E_{1/2}$ vs. molecular weight is shown in Fig. 1. An even more instructive plot is that of $E_{1/2}$ vs. the number of carbon atoms in the substituent chain (Fig. 2). The latter graph demonstrates that the half-wave potential is shifted linearly to negative voltages as a function of the number of carbon atoms in the substituent. The linearity held over the wide range of C_1 to C_6 .

Hydrazine, itself, however, did not fit the curve; extrapolation of the linear portion of the curve to zero carbon atoms gave a value of -0.600 v. which was 52 mv more negative than the experimentally determined value. The data shown in Figs. 1 and 2 may be interpreted in terms of the electron donating properties of alkyl chains. As the chain was increased in length, the half-wave potential for the anodic reaction was shifted negatively, or the oxidation occurred more readily. This increase in ease of oxidation might be explained on the basis of the electron donating effect of increasing alkyl chain length (3). The slope of the line in Fig. 2 corresponded to -31 mv./ carbon atom.

A low value for the diffusion current of nHH was noted. This may be due to a combination of factors including a higher degree of instability in solution, difference in diffusion coefficient, or lessened water solubility. Disubstituted hydrazines, either symmetrical or unsymmetrical, did not appear to fit the same pattern as the monosubstituted compounds (Table I). UDMH and SDMH produced essentially identical half-wave potentials ($\Delta E_{1/2} = 3.4$ mv.) which were shifted negatively from the expected value for a C_2 compound. In addition, based on the diffusion current constant for the monosubstituted hydrazines, the currents for UDMH and SDMH indicated a two-electron reaction rather than a four-electron step. This behavior is similar to that encountered with a platinum electrode in acid medium (5). Di-BH also appeared to undergo only a two-electron oxidation; the half-wave potential was significantly more negative than the methyl substituted compounds, however.

In comparison with the alkyl hydrazines, phenyl hydrazine gave an anodic wave which was shifted positively from that expected for a mono-substituted six carbon hydrazine; the shift was 39.1 mv. In this case, the electron withdrawing character of the benzene ring contributed to produce the positive shift. The lower diffusion current for phenyl hydrazine appears to be due to a difference in diffusion coefficient.

Acetic hydrazide gave an anodic wave which was shifted positively from ethyl hydrazine by 38.8 mv. The disubstituted hydrazide, diacetyl hydrazine, however, was not electroactive over the entire range studied.

LITERATURE CITED

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Table I
POLAROGRAPHIC VALUES FOR SUBSTITUTED HYDRAZINES IN 0.1M NaOH.

Compound	$-E_{1/2}$, v. ^a	i_d , μ a
Hydrazine	0.5475	7.4
Monomethylhydrazine	0.6344	8.0
<u>n</u> -Propyl hydrazine	0.6891	6.0
<u>n</u> -Hexyl hydrazine	0.7907	1.7
1,1-Dimethyl hydrazine	0.6944	4.4
1,2-Dimethyl hydrazine	0.6978	2.7
1,2-Diisobutyl hydrazine	0.7566	4.5
Phenyl hydrazine	0.7516	4.9
Acetic hydrazide	0.6185	7.1
Diacetyl hydrazine	-	-

^a vs. a saturated mercurous sulfate electrode.

Figure 1

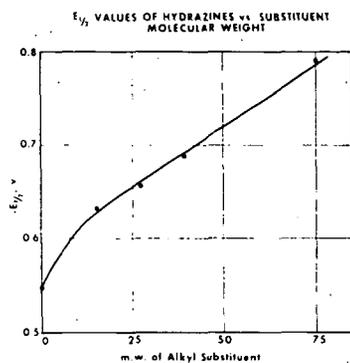


Figure 2

