There is also a large difference in equilibrium constant between the neutral and anion radical states of bianthrone. In the neutral form $K_{AB} = [B]/[A] = 2 \times 10^{-3}$ in dimethylformamide at room temperature.[8] By contrast, $K_{AB}^{-} = [B^{-}\cdot]/[A^{-}\cdot]$ must be very large since the present experiments show that $B^{-}\cdot$ is strongly favored. An estimate of K_{AB}^{-} would be of interest because it is governed in part by the release of steric interaction experienced on going from the doubly folded A form to the twisted B form.

K_{AB}^{-} may be calculated from standard electrode potentials and K_{AB} by eq 5 (see Scheme I for definitions). Both K_{AB} and E_{1B}^{0}

$$\ln K_{AB}^{-} = \ln K_{AB} + (nF/RT)(E_{1B}^{0} - E_{1A}^{0}) \quad (5)$$

(−0.195 V vs. SCE) are available[8] but E_{1A}^{0} cannot be measured directly by electrochemical techniques because the reduction of A is irreversible. As stated earlier, the reduction is thought[8] to proceed by the ECE pathway (electrochemical step/chemical step/electrochemical step), $A \rightarrow A^{-}\cdot \rightarrow B^{-}\cdot \rightarrow B^{2-}$. Assuming that the rate constant for $A^{-}\cdot \rightarrow B^{-}\cdot$ is independent of solvent, the value determined in the present work may be combined with the peak potential observed at a given scan rate in dimethylformamide[8] to calculate E_{1A}^{0}, using the theoretical relationships[20,21] for an ECE process in cyclic voltammetry. The value so obtained is −1.14 V vs. SCE. It may be regarded as a lower limit because the theory pertains to the limit of a very rapid electron-transfer reaction at the electrode and any sluggishness in electron transfer will cause the calculated value to be too negative. When placed in eq 5, a value of $K_{AB}^{-} = 2 \times 10^{13}$ is obtained indicating that the free energy of $A^{-}\cdot$ exceeds that of $B^{-}\cdot$ by 18 kcal/mol.

The fact that $A^{-}\cdot \rightarrow B^{-}\cdot$ ~70 times slower for 1,1′-dimethylbianthrone than for bianthrone itself seems quite reasonable in view of the steric bulk of the methyl groups. The same effect of 1,1-disubstitution is also found for the A → B process in the parent bianthrones.

This latter statement may seem to contradict the repeated observation[4,22] that 1,1′-disubstitution does not impede the reverse B → A process, the reaction whose rate can be measured in the bianthrones. The principal effect of substituents bulkier than fluorine[23] is to destabilize the B form sufficiently to prevent thermochromism, i.e., the energy difference is too large to permit formation of a significant concentration of B at temperatures up to decomposition. Thus 1,1′-disubstitution severely decreases K_{AB} while having little effect on k_{BA}. Consequently, k_{AB} must be decreased by substitution in the 1-positions. Apparently these same effects are found in the anion radicals.

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(20) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706-23.
(21) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 178-90.
(22) Hirshberg, Y.;Fischer, E. *J. Chem. Soc.* **1953**, 629-36.
(23) Bergmann, E. D.; Loewenthal, H. J. E. *J. Chem. Soc.* **1953**, 2572-4.

Comparison of Proton- and Electron-Transfer Equilibria and Rates for Tetraalkylhydrazines

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Abstract: Relative electron-transfer equilibria for 17 tetraalkylhydrazines (R_4N_2) were determined by measurement of their standard potentials for oxidation ($E^{\circ\prime}$) and rates of electron loss by measurement of their standard heterogeneous electron-transfer rate constants (k_s) determined from their cyclic voltammograms. These data are compared with equilibrium and rate constant measurements for proton transfer between R_4N_2 and salicylic acid. All measurements were in dimethyl sulfoxide containing 0.1 M tetraethylammonium perchlorate. Similar trends are found for electron and proton transfer; the most basic R_4N_2 examples are the most easily oxidized and the fastest both to protonate and lose an electron. The proton transfers run under these conditions show anomalous Brønsted behavior; the rate of protonation of R_4N_2 is about twice as sensitive to change of the R groups as is the equilibrium constant, and the rate of deprotonation consequently becomes slower as the reaction becomes more exothermic. A Brønsted-like plot for electron transfers was constructed by estimating the electron-transfer rate constants for all R_4N_2 at the same potential (called k_0); electron transfer also gives anomalous Brønsted behavior for R_4N_2. The electron-transfer rate has been previously shown to be far faster in anti lone pair conformations than in gauche ones, so that electron transfer from acrylic R_4N_2 involves a prior conformational equilibrium to the unstable but rapidly oxidized anti form. It is suggested that a similar gauche to anti conformational change precedes proton transfer under our conditions, and is a major contributing factor to the anomalous Brønsted behavior of R_4N_2.

In a preliminary communication,[1] we reported equilibrium constant and rate constant data for the proton-transfer reactons of tetraalkylhydrazines (R_4N_2) with salicylic acid (HSal), as shown in eq 1, for several α-unbranched examples (alkyl substituents all $R'CH_2-$). The rate constant k_f was measured by a chro-

$$R_4N_2H^+ + Sal^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R_4N_2 + HSal \quad (1)$$

$$K = k_f/k_b$$

noamperometric technique developed for this work[2] in which the potential is stepped to a region where R_4N_2 oxidizes rapidly but the other components of eq 1 are electrochemically inert, and the kinetic current determined. Both the rate and equilibrium constants for eq 1 prove to be quite sensitive to alkyl group structure, and it was proposed that hydrazine conformational effects are reponsible for this sensitivity. We report here additional proton-transfer data for compounds having α-branched alkyl groups (alkyl substituents $R'R''CH-$) and compare the equilibrium and rate constants for proton transfer (eq 1) with those for electron transfer, eq 2, determined by cyclic voltammetry in the same solvent system, dimethyl sulfoxide (Me_2SO) containing 0.1 M

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(1) Nelsen, S. F.; Kinlen, P. J.; Evans, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 1875.
(2) Kinlen, P. J.; Evans, D. H. *J. Electroanal. Chem.*, in press.

tetraethylammonium perchlorate. Relative equilibrium constant data for eq 2 are provided by measuring the formal potential, $E^{\circ\prime}$ (reported vs. AgRE), and the heterogeneous electron transfer rate constant, k_0, for oxidation.

$$R_4N_2 \underset{k_r}{\overset{k_0}{\rightleftharpoons}} R_4N_2^{+\cdot} + e^- \qquad (2)$$

Experimental Section

Reagents. Preparation of the hydrazines has been described.[3] Each was purified by preparative scale gas chromatography (15% XF 1150 on 60/80 mesh Chromsorb W) immediately before use except for compound **22**, which was sublimed. Spectroquality dimethyl sulfoxide (Aldrich) was stored over Linde Type 4A molecular sieves (activated at 300 °C) for at least 24 h. Tetraethylammonium perchlorate was prepared by the method of Kolthoff and Coetzee,[4b] recrystallized from water and vacuum dried. *p*-Toluenesulfonic acid (Eastman) was used as received. Tetraethylammonium salicylate was prepared according to Kolthoff and Chantooni.[4a]

Apparatus. The electrochemical instrumentation, voltammetric cell, and gold disk electrodes were the same as used previously.[2] All potentials are reported with respect to a silver reference electrode (AgRE) composed of a silver wire in contact with 0.010 M silver nitrate and 0.10 M tetraethylammonium perchlorate in Me_2SO. The porous Vycor separator on the AgRE probe has been described.[5] The AgRE assumed a potential of +0.275 V vs. aqueous SCE.

Potentiometric titrations were performed with a glass electrode (Corning 46021), the AgRE, a Leeds and Northrup 7410 pH meter, and an Analogic AN3100 standard voltage source which provided variable offset voltages.

All data were obtained with use of 0.10 M tetraethylammonium perchlorate in Me_2SO at 25.0 ± 0.1 °C.

Procedures. Determination of pK_a of Protonated Hydrazines. Hydrazine (0.1–0.2 mmol) was purified by gas chromatography and collected immediately before each titration. The weighed sample was dissolved (25 mL) and titrated with 0.05 M *p*-toluenesulfonic acid (in Me_2SO plus electrolyte). The volume of titrant required to reach the endpoint and the midpoint (half-titrated) potential were determined from the titration curves. The amount of hydrazine found by titration exceeded 90% theoretical except for compounds **2** (80%), **3** (86%), and **18** (52%).

Each day that titrations were performed, a titration of the reference base, tetraethylammonium salicylate, was carried out. The difference between the pK_a of protonated hydrazine (BH^+) and salicylic acid (HA) was calculated according to the relation:

$$\Delta pK_a = pK_{a,BH^+} - pK_{a,HA} = (E_{h,B} - E_{h,A^-})/0.05915 \qquad (3)$$

where E_{h,A^-} and $E_{h,B}$ are the midpoint potentials observed for titration of salicylate and hydrazine, respectively. The response of the glass electrode was tested in three ways. First, standard solutions of *p*-toluenesulfonic acid (10^{-4}–10^{-1} M) were studied and the slope of plots of potential vs. logarithm of the molar acid concentration was 58 mV. Also, for the titration of tetramethylhydrazine, plots of potential vs. log $(P/(1-P))$, where P is the fraction titrated, were linear with slope of 61 mV. Finally, the pK_a values of four standard acids ranging from pK_a = 4–11 were determined[2] and results were within 0.1 unit of literature values.

Calculation of pK_a for the protonated hydrazines requires a value for pK_a of salicylic acid and a value for the activity coefficients of singly charged ions in Me_2SO/0.10 M tetraethylammonium perchlorate. Kolthoff, Chantooni, and Bhowmik[6] reported pK_a = 6.8 for salicylic acid and extended Debye–Hückel calculations[7] give log $\gamma_\pm = -0.2$ for BH^+ and salicylate. Thus, pK_a for the protonated hydrazines was computed according to the following:

$$pK_{a,BH^+} = 6.8 - 0.4 + \Delta pK_a \qquad (4)$$

Replicate titrations were not performed except for compound **9** for which ΔpK_a = 0.60 and 0.64 were found in two separate experiments. Thus the precision of the ΔpK_a values is probably a few hundreths of a unit. The accuracy of the $pK_{a,BH^{+\cdot}}$ values (±0.1) is limited by the uncertainty in pK_a of salicylic acid and the activity coefficient calculations.

The weakest bases (compounds **20**, **21**, and **24**) did not give discernible endpoints in the titrations.

Determination of $E^{\circ\prime}$. The formal potentials, $E^{\circ\prime}$, for the hydrazine radical cation/hydrazine couples were determined by cyclic voltammetry at a gold disk electrode. Well-formed oxidation and reduction peaks were obtained and the reversible half-wave potential, $E_{1/2}$, was taken as the potential midway between the peaks of a voltammogram recorded at 0.100 V/s. $E_{1/2}$ is related to the formal potential, $E^{\circ\prime}$, by the equation $E_{1/2} = E^{\circ\prime} - (RT/2F) \ln D_{B^{+\cdot}}/D_B$, where $D_{B^{+\cdot}}$ and D_B are the diffusion coefficients of radical cation and hydrazine, respectively.[8] The diffusion coefficients of radical ions are often so similar to those of the neutral parent that $E_{1/2}$ is within a few mV of $E^{\circ\prime}$.[9] In reporting the results it has been assumed that $E^{\circ\prime} = E_{1/2}$.

Typically, replicate voltammograms were recorded and the reproducibility of $E^{\circ\prime}$ was within ±5 mV. In one case (compound **17**) three separate determinations were made over a period of 13 months and the range was only 7 mV.

Determination of Standard Heterogeneous Electron-Transfer Rate Constants, k_s. These are rate constants for the electrode reaction at the standard potential of the couple. They were obtained from the observed anodic/cathodic peak separation in cyclic voltammograms obtained at 0.10 V/s. An extended theoretical working curve was prepared in the manner described by Nicholson.[10] This curve was not very dependent on the anodic electron-transfer coefficient, β_e, and a value of 0.5 was assumed.

In the course of the chronoamperometric determination of protonation rate constants (see next section), values of diffusion coefficients for the hydrazines were obtained. These were of low accuracy due to uncertainties in hydrazine concentration (see discussion of titrations). Therefore, an average value of 6×10^{-6} cm^2/s was employed to obtain the values of k_s from the observed peak separations.[10]

The observed values of $E^{\circ\prime}$ were found to be independent of electrode pretreatment. However, as one often finds with solid electrodes, the experimentally determined k_s values were significantly dependent on pretreatment. In order to obtain reproducible results, the gold surface was lightly polished with an aqueous suspension of 0.1 μm alumina followed by rinsing with water and Me_2SO. This polishing was carried out before obtaining a series of voltammograms of a given compound. Occasionally, it was necessary to polish between voltammograms. Typically, replicate voltammograms yielded k_s values which differed by <30%.

Rate Constants for Reaction of Salicylic Acid with Hydrazines. These rate constants were determined by a chronoamperometric technique described earlier.[2] Briefly, the kinetic current observed for hydrazine oxidation in the presence of excess salicylic acid was obtained. The current–time curves were analyzed to give (in conjunction with ΔpK_a determined above) the forward and reverse rate constants. Studies of tetramethylhydrazine under a number of conditions indicated a precision of about ±25% for the rate constants so determined.[2]

Results

Table I summarizes the proton- and electron-transfer data for 17 tetraalkylhydrazines, as well as the partial results obtained for seven additional compounds. The rate and equilibrium constants are identified in the introduction.

Discussion

Proton-Transfer Equilibria and Rate Constants (Equation 1). The pK_a values of Table I range over greater than 5.4 log units for α-unbranched hydrazines. Larger alkyl groups tend to lower the pK_a of acyclic hydrazines but the relationship is far from regular. Diaziridines **23** (cis alkyl groups) and **24** (trans alkyl groups) are both rather feeble bases, as expected from the decrease in pK_a observed for aziridine relative to larger ring cyclic amines.[11]

The relationship between proton-transfer equilibrium and rate constants is most conveniently examined by inspecting the Brønsted plot shown in Figure 1, a plot of log k_b vs. pK_a, which is a simple x-axis shift from the plot vs. log K^{-1} (see eq 1). The filled circles are for α-unbranched (RCH_2-substituted) compounds, entries 1 to 11 of Table I.[1] This Brønsted plot shows substantial

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[3] (a) Nelsen, S. F.; Hintz, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 7108. (b) Nelsen, S. F.; Peacock, V. E.; Weisman, G. R. *Ibid.* **1976**, *98*, 5269.

[4] (a) Kolthoff, I. M.; Chantooni, M. K. *J. Am. Chem. Soc.* **1963**, *85*, 426. (b) Kolthoff, I. M.; Coetzee, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 870.

[5] Ryan, M. D.; Evans, D. H. *J. Electrochem. Soc.* **1976**, *67*, 333.

[6] Kolthoff, I. M.; Chantooni, M. K.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23.

[7] Kreevoy, M. M.; Wang, Y. *J. Phys. Chem.* **1977**, *81*, 1924.

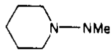
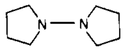
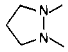
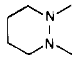
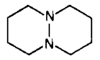
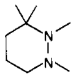
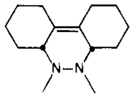
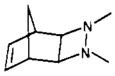
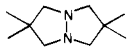
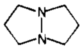
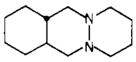
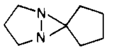
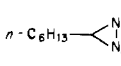
[8] Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

[9] Svanholm, U.; Parker, V. D. *J. Chem. Soc., Perkin Trans. 2* **1975**, 755.

[10] Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

[11] Searles, S.; Tamres, M.; Block, R.; Quaterman, L. A. *J. Am. Chem. Soc.* **1956**, *78*, 4917.

Table I. Data for Acid-Base and Oxidation Reactions of Tetraalkylhydrazines[a]

no.	compound	ΔpK_a[b]	pK_a-($R_4N_2H^+$)	$E^{\circ\prime}$-(Me_2SO),[c] V	$\log k_s$[d]	$\log k_f$[e]	$\log k_b$[e]
1	Me_2NNMe_2	−0.22	6.2	0.102	−2.5	3.5	3.3
2	Et_2NNMe_2	−0.44	6.0	0.085	−3.0	4.2	3.8
3	EtMeNNMeEt	−0.52	5.9	0.118	−3.3	3.0	2.5
4	Et_2NNEt_2	−0.54	5.9	0.119	−3.3	3.5	3.0
5	n-Pr_2NN-n-Pr_2	−1.92	4.4	0.131	−3.8	1.9	0.1
6	i-BuMeNNMe-i-Bu	−1.25	5.2	0.151	−3.8	3.0	1.7
7		−0.24	6.2	0.130	−2.6	4.1	3.9
8		+0.78	7.2	−0.145	−1.8	5.2	6.0
9		+0.62	7.0	−0.082	>−1.7	5.4	6.0
10		+0.64	7.0	0.025	−2.0	4.2	4.8
11		+0.51	6.9	0.085	−1.8	5.3	5.8
12	i-Pr_2NNMe_2	−0.90	5.5	0.093	−3.2	4.3	3.4
13	i-Pr_2NNMe-i-Pr	−1.12	5.3	0.092	−3.4	3.4	2.3
14		+0.93	7.3	−0.126	>−1.7	5.0	5.9
15		−0.22	6.2	+0.020	−2.5	3.0	2.8
16		−0.44	6.0	+0.070	−1.7	5.5	5.1
17		+3.01	9.4	−0.219	−1.8	4.2	7.2
18		+2.28	8.7				
19	Bz_2NNMe	−2.30	4.1	0.280	−3.6		
20	Bz_2NNBz_2		4.0				
21	i-Bu_2NN-i-Bu_2		4.0				
22		+0.49	6.9				
23		−1.67	4.7				
24			4.0				

[a] Solvent: Me_2SO/0.1 M tetraethylammonium perchlorate, 25.0 °C. pK_a values refer to Me_2SO with no electrolyte present. [b] ΔpK_a = pK_a of hydrazine − pK_a of salicylic acid. [c] vs. silver reference electrode, AgRE. [d] Units of rate constant cm s^{-1}. [e] Units of rate constant M^{-1} s^{-1}.

scatter, which is not surprising because the compounds chosen do not minimize steric differences; they were chosen to provide a variety of equilibrium R_4N_2 conformations. The regression line through the filled symbols has a slope β = +2.2 (correlation coefficient r = 0.97, average log k_b deviation 0.34 log units, total range 6.1 units). The rate constant for proton transfer is therefore about twice as sensitive to alkyl-group change in this series as is the equilibrium constant. This is most unusual behavior, as previously pointed out;[1] the Brønsted plot is "anomalous"[12] becase the slope of the plot does not lie between 0 and 1 as is "normal". The reciprocal Brønsted plot (log k_f vs. log K, shown as Figure 1 in ref 1) has a negative slope (its slope, α, must be 1 − β). The deprotonation rate for $R_4N_2H^+$ actually becomes slower as the deprotonation reaction becomes more exothermic.

The open circles of Figure 1 are for α-branched hydrazines, where at least two of the alkyl substituents are of the type R′R″CH. They are seen to roughly follow the trend of the RCH_2-substituent data, although the deviations from the regression line shown are somewhat larger. Steric effects obviously affect reaction rates, but if the bulk of the attached alkyl groups were the principal factor affecting log k_b and pK_a, one would certainly expect to see the α-branched compounds deviating more uniformly from the α-unbranched compounds. Something else besides simple bulk of the alkyl group is the principal factor determining the proton-transfer behavior of R_4N_2.

Compound **17** (the square of Figure 1) has been left for separate discussion, because it is rather clearly a special case. Although it is α-unbranched, it is far more basic than the other compounds, and although it has the largest log k_b measured, it is considerably lower than the α-unbranched correlation line would predict. We suggest that the reason for the deviant behavior of **17** is conformational—**17** is the only hydrazine with syn lone pairs (its lone pair, lone pair dihedral angle θ = 0°)[13] investigated.

We previously suggested[1] a conformational reason for the wide range in pK_a and the anomalous Brønsted behavior of R_4N_2 proton

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[12] Kresge, A. J. In "Proton Transfer Reactions", Caldin, E. F., Gold, V. Eds.; Chapman and Hall: London, 1975; pp 179–99.

[13] Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6982.

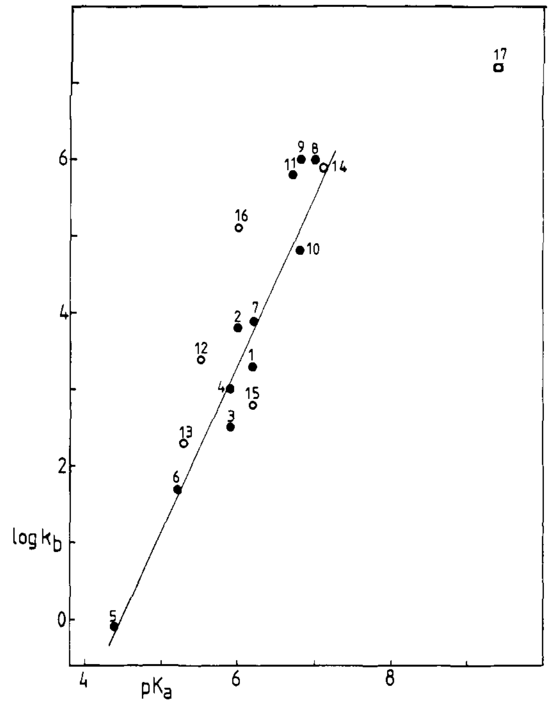

Figure 1. Brønsted plot for hydrazine protonation data, log k_b vs. pK_a. The line drawn is the least-squares line through the filled circles (α-unbranched hydrazines). The open circles are α-branched hydrazines. See Table I for compound identification.

transfers and shall return to this point in the last section.

Electron-Transfer Equilibria and Rate Constants (Equation 2). The $E^{\circ\prime}$ values for a long series of R_4N_2 have been measured previously in acetonitrile,[3,4] and the results discussed in terms of correlation with vapor phase first vertical ionization potentials (IP_1) and geometry changes between neutral R_4N_2 and the cationic $R_4N_2^{+\cdot}$. Figure 2 is a plot of $E^{\circ\prime}$(MeCN) vs. $E^{\circ\prime}$(Me_2SO) for the 16 compounds studied in both solvents. A linear regression gives a correlation coefficient of 0.977 and a slope of 1.04, indicating only a minor solvent effect on the electron-transfer equilibrium. The principal reason for a wide range of $E^{\circ\prime}$ values in a series of R_4N_2 is the large geometry change accompanying electron removal. Steric interactions among the alkyl groups are different in the geometry of neutral R_4N_2 (nitrogen atoms close to tetrahedral, lone pair orbital axes nearly perpendicular ($\theta \sim 90°$) in acrylic compounds) and of $R_4N_2^{+\cdot}$ (nitrogen atoms close to planar, parallel p orbitals bearing the three remaining "lone pair" electrons). These steric interactions are not expected to vary significantly with solvent, so the rather good $E^{\circ\prime}$(MeCN), $E^{\circ\prime}$(Me_2SO) correlation observed is reasonable.

The correlation is clearly far from perfect, and we turn our attention now to the deviations from linearity. Acyclic compounds **1–6**, **12**, and **13** all have similar conformations about the NN bond, $\theta \sim 90°$, in the neutral form. When only compounds containing normal alkyl groups are considered, so that steric changes are similar, a rather smooth decrease of $E^{\circ\prime}$(MeCN) occurs as the alkyl groups are lengthened and IP_1 decreases. The decrease in $E^{\circ\prime}$ is substantially less than in IP_1 because most of the IP_1 decrease is caused by alkyl group polarization in the cation, an effect which nearly disappears in solution, where solvent is available for polarization. The slope of an $E^{\circ\prime}$(CH_3CN) vs. IP_1 plot for *n*-alkylhydrazines is about 0.15. A solvent effect might also be contributing to the low slope.[3,14] If longer alkyl groups shielded solvent from the region of the polar nitrogens, $R_4N_2^{+\cdot}$ with larger alkyl groups would be preferentially destabilized and the slope would be lowered. Although such an effect was barely discernible in the $E^{\circ\prime}$(MeCN) data, the scatter observed for **1–6**, **12**, and **13** make such an effect appear more important in Me_2SO. For example Et_4N_2 and *n*-Pr_4N_2 are 0.017 and 0.031 V harder to oxidize than Me_4N_2 in Me_2SO, although they have lower vapor phase IP_1 and their $E^{\circ\prime}$(MeCN) values are lower. It is difficult to treat this effect quantitatively, but we suggest that less effective solvation of $R_4N_2^{+\cdot}$ brought about by exclusion of solvent by large alkyl groups is reasonably more important for the bulkier, branched solvent Me_2SO than for MeCN, and is an important contributing factor to the rather modest scatter apparent in Figure 2.

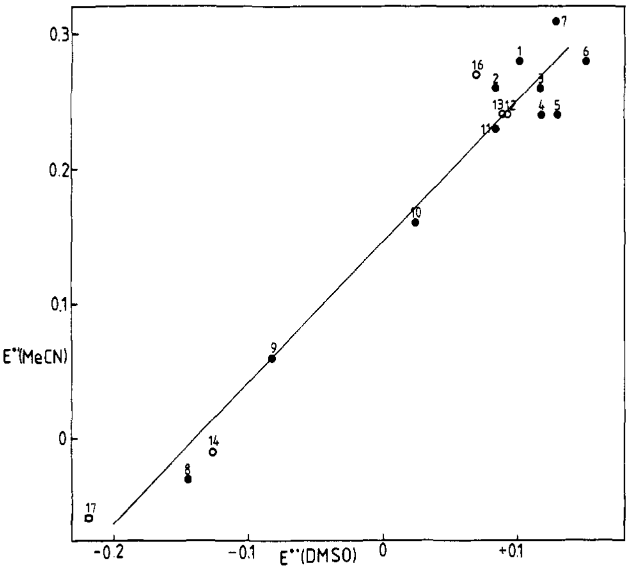

Figure 2. Plot of $E^{\circ\prime}$(MeCN), data in acetonitrile containing 0.1 M sodium perchlorate, referenced to SCE, vs. $E^{\circ\prime}$(Me_2SO), data in dimethylsulfoxide containing 0.1 M tetraethylammonium perchlorate, referenced to AgRE.

Inspection of Table I will show that there are some obvious similarities between proton- and electron-transfer equilibrium and rate constants. The most basic hydrazines are also the most easily oxidized and the fastest to both protonate and lose an electron. To allow a reasonable comparison of the proton- and electron-transfer processes, we would like to generate a Brønsted-like plot for electron transfer analogous to the Brønsted plot of Figure 1.

In order to prepare such a plot, the logarithm of the rate constant for oxidation, k_0 in reaction 2, must be measured at a given electrode potential and be plotted vs. the logarithm of the electron-transfer equilibrium constant, K_e, at the same potential. We have selected the $Me_4N_2^{+\cdot}/Me_4N_2$ standard potential as the reference potential. (This is analogous to using salicylic acid as the reference acid in the protonation studies). K_e is the equilibrium constant for electron-transfer reaction 5. It is obtained from the differences in $E^{\circ\prime}$ for the hydrazines.

$$R_4N_2 + Me_4N_2^{+\cdot} \rightleftharpoons R_4N_2^{+\cdot} + Me_4N_2 \qquad (5)$$

The k_s values correspond to the rate constant k_0 at the $E^{\circ\prime}$ value for each hydrazine. To calculate the value of k_0 at the reference potential, $E^{\circ\prime}$ for Me_4N_2, we use the relationship between k_0 and potential[15]

$$\log k_0 = \log k_s + \frac{\beta_e F}{2.303RT}[E^{\circ\prime}(Me_4N_2) - E^{\circ\prime}(R_4N_2)] \qquad (6)$$

where β_e is the anodic electron-transfer coefficient. Values of β_e close to 0.5 are expected for simple electron-transfer reactions and this value was selected to calculate values of k_0.

Figure 3 shows the Brønsted-like plot of log k_0 vs. log K_e for the data of Table I. Comparison of proton- and electron-transfer processes as in Figures 1 and 3 is apparently novel, though the relationship between the antecedents to eq 6 and the Brønsted relation from proton transfer was recognized at an early date.[16]

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(15) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods, Fundamentals and Applications"; John Wiley and Sons; New York, 1980, p 95.

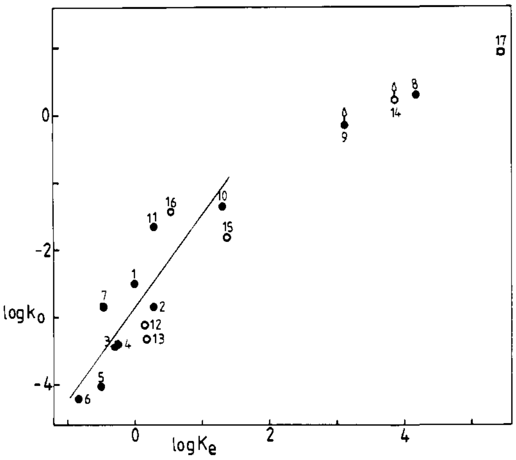

Figure 3. Brønsted-like plot for hydrazine electron-transfer data, log k_0 vs. log K_e. The line drawn is the least-squares line through the filled circles (α-unbranched hydrazines). The open circles are α-branched hydrazines. See Table I for compound identification.

There is an experimental problem at the high k_0 end of the plot because the cyclic voltammetric peak potential separation is close to the reversible limit so only a lower limit on k_s has been obtained for some compounds (designated as log $k_s > -1.7$ in Table I). The use of faster scan rates would be necessary to extend the range but even then only about a factor of 10 in k_s would be gained.[17] Thus, the entries for **9** and **14** are only minimum values and those for **8**, **11**, and **17** might well be substantially in error. The regression line rather arbitrarily drawn in Figure 3 is for the α-unbranched compounds of log $k_s < -1.7$, **1**–**7**, **10**, and **11** (corresponding to that drawn in Figure 1), which has $r = 0.87$, slope 1.37, average log k_0 deviation 0.41, and total range 2.88 units.

There is obviously even more scatter in Figure 3 than in Figure 1, and the slope of the rather poor regression line of Figure 3 is lower than that of Figure 1, but we believe it is worth pointing out that for the electron transfer as well as for the proton transfer, the rate appears to be more sensitive to substitution change than is the equilibrium constant. Thus, the electron transfer, like the proton transfer, is a reaction which gives anomalous Brønsted behavior. This is not surprising because we have shown earlier that hydrazine oxidation occurs preferentially for certain conformations so substantial structural change will precede electron transfer.[18]

It should be emphasized that the structural dependence of the k_0 values for the hydrazines is quite exceptional. Brønsted-like plots prepared from k_s values and $E^{\circ\prime}$ reported for the reduction of nitro compounds[19] and aromatic compounds[20] were found to have normal slopes, well below unity. A "normal" slope will be obtained whenever k_s is not strongly dependent on K_e (i.e., on $E^{\circ\prime}$). In most families of structurally related compounds the dependence is weak, but such is not the case with the tetraalkylhydrazines.

The β_e values were not determined and were assumed to be 0.5 for each compound. The slope of Figure 3 would be increased if the true value of β_e tended to be greater than 0.5 and decreased if less than 0.5. If β_e were as small as 0.3, the slope would be decreased by only 0.2 unit and would still be anomalous. In cases where k_s was small, the value of β_e could be estimated from the shape of the voltammograms and it was clearly >0.3.

Alternatively, the slope of Figure 3 could be affected if β_e were potential dependent.[21] For some reactions it has been found that β_e is close to 0.5 at $E^{\circ\prime}$ but decreases slightly at more positive potentials. However, inclusion of the largest potential dependence yet observed,[21] 0.5 V^{-1}, would only reduce the slope of Figure 3 by 0.1 unit.

Finally, the k_s values of Table I have not been corrected for double layer effects. For positive values of $E^{\circ\prime}$ the potential at the reaction site, ϕ_r, will be slightly more positive than the bulk solution potential which results in the measured k_s values being lower than the true values. Equation 7 may be used to calculate

$$k_{s,\mathrm{true}} = k_s \exp(\beta_e F \phi_r / RT) \qquad (7)$$

corrected values. However, evaluation of ϕ_r requires double layer data which is scarce for nonaqueous solvents with mercury electrodes[21,22] and almost nonexistent for solid electrodes. Still, it seems quite unreasonable to attribute the anomalous slope of Figure 3 to double layer effects. A change of ϕ_r of 90 mV would be required over the 126 mV $E^{\circ\prime}$ range of the points used in Figure 3 in order to bring the slope down to 1.0. From the available data[21,22] such a strong dependence of ϕ_r on E is exceedingly unlikely for 0.10 M electrolyte.

Conformational Effects on Hydrazine Reactivity. Comparison of Figures 1 and 3 will demonstrate a noteworthy parallelism between alkyl group effects on electron- and proton-transfer reactions of R_4N_2. These plots are certainly not identical. The x axis spread in log K_e is larger than the spread in pK_a (especially when the obviously differently behaving $\theta = 0°$ point **17** is not considered). This is not surprising, because we know that a greater geometry change is involved in the electron transfer. The nitrogens of a neutral hydrazine are nearly tetrahedral, and the lone pair–lone pair dihedral angle θ is about 90° for the acyclic and *N*,*N*-cycloalkyl compounds studied here. The cation radical has nearly planar nitrogens and a θ value of 0°/180° (they are the same for planar nitrogens). In the proton-transfer product, the nitrogens are certainly expected to remain nearly tetrahedral, so alkyl group steric interaction changes during the proton-transfer reaction cannot be as large as they are in the electron-transfer reaction. We will argue that the principal reason for the parallel and quite unusual appearance of Figures 1 and 3 is that the θ = 180° conformation of R_4N_2 is the reactive one in both the electron- and proton-transfer reactions.

It is worth pointing out first that a simple electron transfer without important conformational effects does not fit our electron-transfer rate data at all reasonably. In an important study of tetraalkylmetal oxidation reactions, Klinger and Kochi[23] demonstrated that the electron-transfer rate is essentially completely controlled by the driving force for one-electron oxidation. Heterogeneous rate constants for electron transfer at a given potential (called k_E in the Klinger–Kochi paper and k_0 here) were measured for twelve R_4M compounds (M = Si, Ge, Sn, Pb, Hg), and as is implicitly obvious from their discussion, there is an excellent correlation between log k_E and vapor-phase ionization potential. For example, a plot of their log k_E values at 0.984 V (ref 23, Table VI, column 5) vs. vertical ionization potential (Table I, column 4) has a high correlation coefficient ($r = -0.965$), and the average log k_E deviation is 0.42 log unit (out of a total range of 6.66 units), despite the variation of the central metal and of the alkyl groups all the way from methyl to *tert*-butyl and *neo*-pentyl. Such a plot for R_4N_2 data shows virtually no correlation; log k_0 vs. IP_1 for the 11 available hydrazines with log K_e below 1.7 (IP_1 is not available for **15**) has a correlation coefficient of only $r = -0.20$, and the average deviation of 0.70 log k_0 unit (out of a range of 2.88 units). Neither electron-transfer rate (measured by k_0) nor equilibrium constant (measured by $E^{\circ\prime}$) correlate well with IP_1, because a large geometry change occurs during electron transfer.

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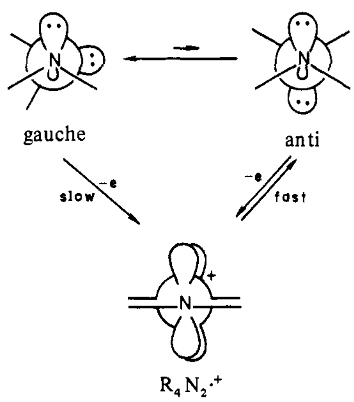
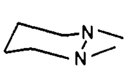
Scheme I

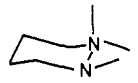


The correlation of rate with equilibrium constant shown in Figure 3 is better, but shows anomalous Brønsted behavior, in qualitative analogy with the proton transfers.

The importance of conformational change in the electron loss for six-membered ring cyclic hydrazines has considerable independent support. We have shown empirically by low-temperature CV studies that the $\theta \sim 180°$ diequatorial alkyl group conformations ee have much larger heterogeneous electron-transfer rate constants than $\theta \sim 60°$ axial, equatorial alkyl group conformations ae.[18] The ee and ae oxidation waves are kinetically resolved, the irreversible ae wave appearing at higher potential than the ee wave, even when the ae conformation is more stable than the ee conformation so that $E°'$ (ae, radical cation) is negative of $E°'$ (ee, radical cation). Observation of different oxidation waves for different conformations requires slow interconversion of ee and ae in solution on the CV time scale, which can be attained at low temperatures and/or fast scan rates. The ee,ae k_s difference has not been accurately measured because of substantial experimental problems, but must be at least three orders of magnitude to give the observed results. These experiments lead us to expect that the mechanism for electron loss from acyclic hydrazines, which exist overwhelmingly in the unreactive $\theta \sim 90°$ conformation (gauche) involves prior rotation to an unstable conformation with parallel lone pairs (anti), which rapidly loses an electron, as indicated in Scheme I. We suggest that the prior equilibrium to the unstable but more reactive anti conformation provides the qualitative explanation for the anomalous Brønsted-like plot of Figure 3 and the lack of log k_0 vs. IP_1 correlation. Larger alkyl groups would presumably lower the ratio of anti to gauche conformations, contributing to the k_0 pattern observed. Solvation changes destabilizing $R_4N_2^+\cdot$ relative to R_4N_2 as the alkyl groups become longer presumably also influence the plot significantly.



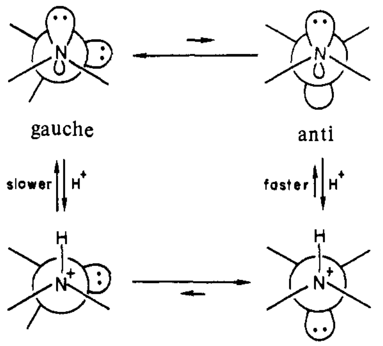
ee



ae

We previously suggested[1] an analogous NN bond rotation to explain the anomalous Brønsted plot for the proton-transfer reactions. This is written out explicity as Scheme II for an acyclic ($\theta = 90°$) hydrazine. If anti were more basic than gauche and protonated more rapidly, the gauche,anti prior conformational equilibrium would precede protonation of acyclic R_4N_2. Following the prior equilibrium pathway would require using an acid of comparable acidity to $R_4N_2H^+$, so that protonation of gauche (which will certainly occur rapidly when the reaction is highly exothermic) will not be too fast. These are precisely the conditions used for the proton-transfer study, where salicylic acid is the protonating species.

Scheme II



The qualitative similarity of Figures 1 and 3 provides further support for Scheme II, because there is excellent independent evidence for Scheme I, as discussed above.

Scheme II suggests that anti is kinetically and thermodynamically more basic than is gauche, a result which seems reasonable to us on various grounds. It will be noted from Table I that the bicyclic hydrazine **11**, which is exclusively in the anti conformation,[16c] is 1 pK unit more basic than is tetraethylhydrazine **4**, which is all gauche at equilibrium, and also that the log k_b of **11** is 1.8 units higher than that of **4**. Such a reactivity difference is entirely in concert with the qualitative lone pair stereochemistry arguments of Deslongchamps,[24] although his work refers to very different systems and reactions. Furthermore, we know from X-ray crystallographic studies that the geometry at nitrogen of ee R_4N_2 is more bent than that of ae R_4N_2, so that the lone pairs of the former have higher s character, which ought to facilitate NH bond formation. The suggested favoring of the anti HN^+,Nlp conformation (Nlp stands for nitrogen lone pair) for R_4N_2H in Scheme II is a suggestion that an anomeric effect[26] is important. Experimental evidence for a significant RN^+,Nlp anomeric effect has come from low-temperature ^{13}C NMR studies of pentaalkylhydrazine cations,[17] but no experimental data are yet available on whether RN^+ or HN^+ interaction is larger. Because we believe the σ^* orbital to be clearly lower in energy for the HN^+ than the RN^+ bond, leading to greater stabilization when HN^+ is anti to Nlp, we have written the equilibrium as favoring this species.

Conclusion

This study provides support for a conformation-dependent reactivity enhancement for both electron loss from and proton addition to tetraalkylhydrazines in which the electronically destabilized anti form is the more reactive conformation. Our results have obvious implications for considering the "α effect",[28] in which species with adjacent lone pairs are found to exhibit anomalously great nucleophilicity.

Acknowledgment. We thank the National Science Foundation for partial support of this work through Grants CHE 77-24627 and CHE-78-08727.

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(24) For a review of this work, see: Deslongchamps, P. *Heterocycles* **1977**, *7*, 1271 and references therein.

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