# Nitrogen Inversion of Tertiary Amines in Aqueous Acid[1]

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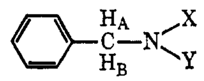
**Abstract:** The kinetics of the nitrogen inversion of three tertiary amines have been studied in aqueous acid solution utilizing high-resolution nuclear magnetic resonance. Line-shape analysis of the AB nmr pattern of methylene protons on each compound provided a measure of the rate of interchange of the magnetic environments of these protons which results upon the reprotonation of the free base following an odd number of inversions. The inversion rate was found to follow a modification of the first-order protolysis reaction given by Grunwald. Inversion rate constants of $10^8$–$10^9$ sec$^{-1}$ are estimated. These are compared to inversion rate constants for nitrogen atoms contained in ring systems. A second-order dependence of inversion upon the concentration of amine was also found. The rate law for this inversion process follows very closely the second-order proton exchange reaction for the amine in question. Application of solvent isotope effects to the protolysis rate parameters predicted the observed results of nitrogen inversion in $D_2O$ solutions.

For years a considerable effort was dedicated to attempts to resolve optical isomers of trivalent nitrogen compounds with no success.[2] On the basis of theoretical calculations, Kincaid and Henriques predicted that no resolution of the optical isomers of trivalent nitrogen compounds could be obtained at room temperature and that substituted ethylenimines offered the best possibility at low temperatures.[3] These authors predicted an activation energy for inversion of approximately 25 kcal/mol for ethylenimines and 15 kcal/mol for trimethylamine, which can be compared with 8 kcal/mol for ammonia in the gas phase. Bottini and Roberts found that the nitrogen inversion of aziridines could be slowed to a sufficiently low rate to permit the observation of the nuclear magnetic resonance spectra of the two isomers.[4] However, these authors found the predicted activation energy to be somewhat high. Kincaid and Henriques considered the substituent effect on the inversion activation energy for amines and concluded that substitution of larger groups lowered the activation energy.[3] This result was attributed to an increase in the energy of the pyramidal structure as a result of steric interactions, whereas little change was predicted in the energy of the planar structure.

Griffith and Roberts obtained a resolved spectrum of N-benzyl-O,N-dimethylhydroxylamine below −70° in several aprotic solvents.[5] These authors found that the activation energy for inversion varied inversely with the dielectric constant of the solvent, and attributed this to differences in the dipole moment of the pyramidal and planar structure of the amine. An earlier determination of the inversion rate of ammonia[6] using microwave spectroscopy and the work of Griffith and Roberts indicated that the rate of inversion of acyclic amines is in most cases too fast to be studied by high-resolution nuclear magnetic resonance. Fortunately, Saunders and Yamada introduced a technique which made the study of nitrogen inversion of certain tertiary amines in aqueous solution accessible by nmr.[7] The method is based upon the assumption that a protonated tertiary amine cannot undergo inversion. By varying the acidity of the aqueous solution of the amine, the fraction of the amine in solution which is protonated can be controlled. Because the rate of proton exchange is very fast, all amine molecules in the solution are rapidly converting between a protonated and unprotonated state. However, the overall effect is to reduce the averaged rate of inversion of each molecule to a value which can be measured by nmr. The signal which detects the inversion is the interchange of two methylene protons which are nonequivalent in one isomer and interchange their magnetic properties upon inversion. An example of amines which can be studied is the structure



where X and Y are not identical groups and are not protons. Either X or Y may be a benzyl group. In the limit of slow inversion, the methylene protons give rise to an AB nuclear magnetic resonance spectrum. In the event that the N–H proton exchange is also slow, then spin coupling between the N–H and methylene protons will result in an ABX pattern.[8] As the inversion rate is increased by reducing the acidity of the solution, the nonequivalence of the methylene protons is averaged by rapid interconversion and the AB pattern coalesces to a single peak. The rate of this AB interchange can be determined by line-shape analysis of the nmr spectrum.[9]

Saunders and Yamada calculated the rate of inversion of N,N-dibenzylmethylamine using the expression

$$1/\tau = k_{\text{inv}}\frac{[B]}{([BH^+] + [B])} \qquad (1)$$

where [B] is the concentration of unprotonated amine and [BH+] is the concentration of the amine salt. Ac-

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[1] This investigation was supported by Public Health Service Grant No. GM-13935 from the National Institutes of Health.

[2] H. Gilman, "Organic Chemistry, an Advanced Treatise," Wiley, New York, N. Y., 1938, Chapter 3.

[3] J. F. Kincaid and F. C. Henriques, Jr., *J. Amer. Chem. Soc.*, **62**, 1474 (1940).

[4] A. T. Bottini and J. D. Roberts, *ibid.*, **78**, 5126 (1956); **80**, 5203 (1958).

[5] D. L. Griffith and J. D. Roberts, *ibid.*, **87**, 4089 (1965).

[6] D. H. Whiffen, "Spectroscopy," Wiley, New York, N. Y., 1966, p 84.

[7] M. Saunders and F. Yamada, *J. Amer. Chem. Soc.*, **85**, 1882 (1963).

[8] W. F. Reynolds and T. Schaffer, *Can. J. Chem.*, **42**, 2119 (1964).

[9] (a) J. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958); (b) S. Alexander, *ibid.*, **37**, 966 (1962).

cording to eq 1, the inversion rate constant is given by $k_{\text{inv}}$ and $1/\tau$ is the observed specific rate of inversion. The measurements are usually made using solutions much more acidic than the p$K_a$ of the amine salt so that the assumption [B] $\ll$ [BH$^+$] is valid and eq 1 can be approximated as

$$1/\tau = k_{\text{inv}}\frac{K_a}{[\text{H}^+]} \tag{2}$$

where $K_a$ is the dissociation constant for the amine salt. It is the purpose of this report to show that the proton exchange rate can influence the experimental results when nitrogen inversion rates are determined using the technique of Saunders and Yamada. A central point will be to show that the relationship between the rate of inversion so measured and pH is governed by the relative values of characteristic proton exchange parameters for the amine in question. The compounds used in this study are N,N-dibenzylmethylamine (DBMA), N-benzyl-N-methyl-2-chloroethylamine (BMEClA), and N-benzyl-N-methylethanolamine (BMEA).

## Experimental Section

All amines with the exception of BMEClA were obtained from Aldrich Chemical Co. and were purified by vacuum distillation. BMEClA was prepared from BMEA by refluxing the hydrochloride of BMEA with thionyl chloride. The product was confirmed by infrared and nmr spectra. The product was easily converted to BMEA in aqueous solution above pH 7 but was stable in aqueous hydrochloric acid.

Stock solutions were prepared from the pure amines, except for BMEClA which was prepared from the hydrochloride, and were diluted to the desired amine concentration. Acid concentrations were adjusted by means of pH measurement in the individual samples. Amine concentrations were 0.75 *M* unless stated otherwise and the acidity ranged from pH 1 to 5. Dissociation constants of the amine salts were determined by differential potentiometric titration.[10]

$D_2O$ solutions were made by the procedures given above except that the pH was adjusted using standard DCl or KOD. Corrections to the pD scale were made by adding 0.40 to the pH meter reading. DCl solutions were prepared by distilling DCl gas, produced from the reaction of benzoyl chloride and $D_2O$, into $D_2O$ until the desired concentrations were obtained. KOD solutions were prepared by treating potassium metal with $D_2O$. Both DCl and KOD were prepared and stored under a nitrogen atmosphere. The % H in these solutions was determined by standard additions of $H_2O$ to the solutions followed by integration of the HDO nuclear magnetic resonance line. Back extrapolation of a plot of area *vs.* added $H_2O$ yields the % H present in the $D_2O$ samples. In all cases the % H was 0.3% or less.

Nuclear magnetic resonance data were obtained on a Varian Associates HA-100 nuclear magnetic resonance spectrometer operated under slow passage conditions. Routine checks were made to ensure against saturation of the spectra. Temperature was regulated at 25 ± 1° using a Varian variable temperature probe. All data were treated with standard least-squares techniques.

Rate parameters were obtained by comparison of computer simulated line shapes with experimental ones. The simulated residence time $\tau$ of a proton before A–B interchange was adjusted so that a minimum standard deviation between computed and experimental points on the spectra was obtained. The program used was prepared utilizing the equations of Alexander[9b] and was checked against a similar program obtained indirectly from Saunders. Both programs included compensation for the line width of the spectra in the absence of inversion. In all cases $\tau$ was determined using the line shape of the methylene proton resonance in the compounds studied. These patterns are found at approximately 5 ppm relative to tetramethylsilane. The value of the line width in the absence of kinetic processes was assumed to be a result of magnetic field inhomogeneities and was found to be about 1.1–1.3 cps in most cases. In $H_2O$ solutions care was taken not to make measurements on spectra in cases in which ABX character was introducing additional broadening. The spin coupling constants $J_{AB}$ and chemical shift values $\Delta\nu_{AB}$ are found in Table I.

**Table I.** Nmr Parameters for Compounds Studied

| | $J_{AB}$ | $\Delta\nu_{AB}$ |
|---|---|---|
| DBMA | 13.26 | 11.05[a] |
| BMEA | 13.25 | 15.39 |
| BMEClA | 13.90 | 12.81 |

[a] This chemical shift was found to be very concentration dependent. The value shown was determined using a 0.5 *M* solution of DBMA. The values used in the line-shape analysis were interpolated from a working curve.

## Results and Discussion

In order to develop the results presented here, it is first desirable to examine some of the properties of the earlier treatment of nitrogen inversion in aqueous acid. After taking the logarithim of both sides of eq 2, a plot of log $1/\tau$ for AB interchange *vs.* pH should result in a straight line with a slope of unity and an intercept of log ($K_ak_{\text{inv}}$). Such plots for N,N-dibenzylmethylamine (DBMA), N-benzyl-N-methyl-2-chloroethylamine (BMEClA), and N-benzyl-N-methylethanolamine (BMEA) are shown in Figures 1, 2, and 3, respectively. In the cases of DBMA and BMEClA in the range of inversion rates accessible by nmr, plots which at first appeared linear were observed. However, slopes of 0.64 and 0.76, respectively, were obtained. A similar plot for the inversion rate of BMEA displayed a more definite deviation from the predictions of eq 2. Above pH 3.5 the plot is linear with a slope of unity; however, below pH 3.5 the plot curves to a slope approaching zero. The results for this compound at the lower end of the experimental region suggest that the slope may again become more positive. On the basis of the results found for BMEA, a closer inspection of the data for DBMA and BMEClA led us to question the assumed linearity of the plots for the latter compounds. This deviation from the linear plots predicted by eq 2 suggests that the observed rate of nitrogen inversion of these amines is controlled by some factor other than the simple acid–base dissociation reaction upon which the equation is based. Consideration of the details of the protolysis reactions of amines is required.

The proton exchange kinetics of the compounds discussed in this report have been studied.[11] A comparison of the rate of proton exchange of BMEA with the rate of AB interchange in the pH range 1–2 shows that the rate of interchange is very close to the rate of N–H proton exchange in this region. This observation indicates that there is at least one inversion for each proton exchange and that the observed rate of nitrogen inversion may be controlled in part by the mechanism of proton exchange in this pH region. The mechanism for proton exchange of tertiary amines has been shown repeatedly to follow a scheme represented by eq 3–5.[11,12] Equations 3 and 4 represent a two-step, first-order proton exchange and eq 5 represents a bimolecular proton transfer between the salt and free

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[10] A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, *J. Org. Chem.*, 20, 747 (1955).

[11] D. E. Leyden and W. R. Morgan, *J. Phys. Chem.*, **73**, 2924 (1969).

[12] E. K. Ralph, III and E. Grunwald, *J. Amer. Chem. Soc.*, **89**, 2963 (1967), and references therein.

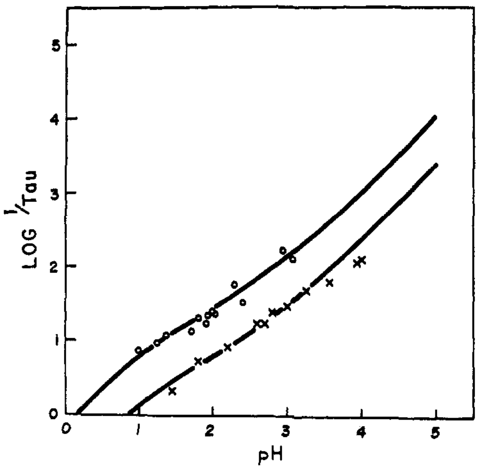


Figure 1. Log rate of nitrogen inversion *vs.* pH and pD for DBMA: ○, 0.75 *M* DBMA in $H_2O$; ×, 0.75 *M* DBMA in $D_2O$.

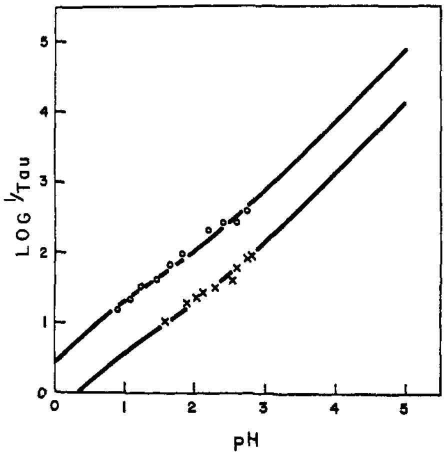


Figure 2. Log rate of nitrogen inversion *vs.* pH and pD for BMEClA: ○, 0.75 *M* BMEClA in $H_2O$; ×, 0.75 *M* BMEClA in $D_2O$.

base through a water molecule bridge. Other mechanisms are possible but generally not as important as these two. Application of a steady-state approximation to the concentration of B···HOH in eq 3 and 4 and consideration of eq 5 lead to a combined first- and second-order rate expression for proton exchange given by eq 6.

$$BH^+\cdots HOH + H_2O \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} B\cdots HOH + H_3O^+ \qquad (3)$$

$$B\cdots HOH \xrightarrow{k_H} B + HOH \qquad (4)$$

$$BH^+\cdots \underset{H}{O}\text{-}H + B \xrightarrow{k_2} B + H\text{-}\underset{H}{O}\cdots HB^+ \qquad (5)$$

$$1/\tau = \frac{\text{rate}}{[BH^+]} = \frac{k_ak_H}{k_H + k_{-a}[H^+]} + \frac{k_2K_a[BH^+]}{[H^+]} \qquad (6)$$

The parameters in eq 6 have been determined by us for the three compounds discussed here[11] and by Grunwald and Ralph for DBMA.[13] Consideration of the above mechanism reveals that the dissociation of the ammonium proton does not lead to a species which is likely to undergo inversion; the B···HOH species is well defined by the analysis of the kinetic data. The earlier assumption that the effective rate of inversion (AB interchange) will be determined by the mean lifetime of the inverting species is valid. However, eq 6 shows that the mean lifetime of that species is not related to acidity of the solution in the manner upon which eq 2 is based. Also, the possible influence of the second-order mechanism is brought into view. The latter process effectively reduces the mean lifetime of the deprotonated amine, but may in addition promote inversion. Although many combinations of values of the parameters in eq 6 are possible, the most general case predicts an increase of the proton exchange rate with pH at low pH values, a pH-independent region while $k_H \gg k_{-a}[H^+]$ and the second-order reaction is negligible, and finally an increase with pH as the second term in the equation becomes large compared with $k_a$. Part of this shape is recognized in the plot of the BMEA data in Figure 3.

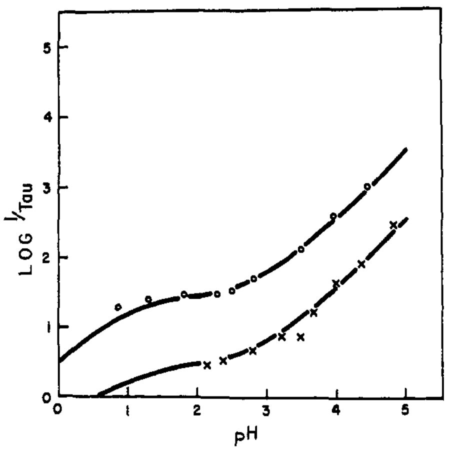
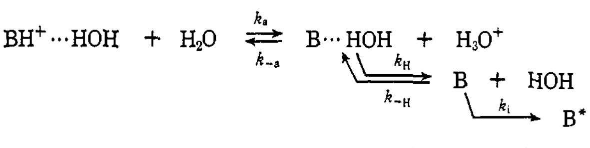


Figure 3. Log rate of nitrogen inversion *vs.* pH and pD for BMEA: ○, 0.75 *M* BMEA in $H_2O$; ×, 0.75 *M* BMEA in $D_2O$.

If eq 3 and 4 are reconsidered as processes leading to the formation of a species capable of inversion, a sequence of reactions may be written as shown in eq 7, where B* represents an inversion of B. The rate of this process may be described by eq 8, in which $1/\tau_i$ represents the observed rate of AB interchange, $k_i$ is the inversion rate constant, and $k_{-H}$ a pseudo-first-order rate constant of rehydration (and/or reprotonation) of the amine. An analogous expression has been presented by Johnson, in which the reactions represented by eq 3 and 4 are assumed to be a one-step process.[14] The equations given by Johnson can be shown to be identical with eq 2 if the system is assumed to be at equilibrium and the rate of inversion is assumed to be slow compared to the rate of reprotonation of the amine.



(7)

$$BH^+\cdots HOH + H_2O \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} B\cdots HOH + H_3O^+;\quad B\cdots HOH \underset{k_{-H}}{\overset{k_H}{\rightleftharpoons}} B + HOH;\quad B \xrightarrow{k_i} B^*$$

$$1/\tau_i = \left(\frac{k_ak_H}{k_H + k_{-a}[H^+]}\right)\left(\frac{k_i}{k_i + k_{-H}}\right) \qquad (8)$$

If $k_i \ll k_{-H}$ eq 8 may be approximated by eq 9. In

$$1/\tau_i = \left(\frac{k_ak_H}{k_H + k_{-a}[H^+]}\right)\left(\frac{k_i}{k_{-H}}\right) \qquad (9)$$

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[13] E. Grunwald and E. K. Ralph, III, *J. Amer. Chem. Soc.*, **89**, 4405 (1967).

[14] C. S. Johnson, Jr., *Advan. Magn. Resonance*, **1**, 74 (1965).

**Table II.** Kinetic and Equilibrium Parameters

| Compound | $pK_a^H$ | $pK_a^D$ | $k_H$ | $k_a$ | $k_{-a}$ | $\frac{k_i}{(k_i + k_{-H})}$ | $k_2$ |
|---|---|---|---|---|---|---|---|
| BMEA | 8.41 | 9.12 | $1.2 \times 10^9$ | 34 | $8.8 \times 10^9$ | 1.3 | $2.8 \times 10^7$ |
| DBMA | 7.92 | 8.58 | $2.8 \times 10^9$ [a] | 120 | $1 \times 10^{10}$ [b] | 0.24 | $1.5 \times 10^7$ [a] |
| BMEClA | 7.30 | 7.96 | $5.3 \times 10^8$ | 500 | $1 \times 10^{10}$ [b] | 0.11 | $2.9 \times 10^7$ |

[a] Reference 13. [b] Estimated.

this case, the observed inversion rate will be some fraction of the rate of proton exchange given by the mechanism represented by eq 3 and 4. On the other hand, if $k_i \gg k_{-H}$ eq 8 becomes identical with the first term in eq 6; the rate of inversion will be equal to the rate of proton exchange by the first-order mechanism. Qualitatively it can be recognized that if many inversions occur before the amine is rehydrated (and reprotonated), there is an equal probability of obtaining the original and inverted enantiomer. Therefore, the observed rate of AB interchange will be one-half the rate of proton exchange. In this event, $k_i$ cannot be evaluated.

Figure 4 shows a plot of $1/\tau_i$ for the AB interchange *vs.* the concentration of BMEA and DBMA. These plots are significant because they show that the rate of interchange of the methylene protons is second order in the concentration of the amine salt at the pH values at which the data were obtained. Added inert salts do not give this result. Moreover, a rate constant analogous to $k_2$ in eq 6 was calculated from the slopes of these plots to be $2.8 \times 10^7$ and $2.9 \times 10^7$ $M^{-1}$ sec$^{-1}$, respectively, for BMEA and DBMA. These values are in agreement with $1.5 \times 10^7$ $M^{-1}$ sec$^{-1}$ for DBMA determined at similar concentrations by Grunwald and Ralph using spin-echo techniques.[18] The value of $k_2$ previously determined by us for DBMA was larger; this was attributed to the high acid and salt concentrations required for measurement by high-resolution techniques.[11] The values of $k_2$ for BMEA and BMEClA could not be determined from the methyl resonance because the spectral lines became sharp below the pH required for the rate of the second-order mechanism to become significant. The correlation between the concentration dependence of the observed rate of AB interchange and the above discussions leads to a proposal of the following rate expression for the inversion of tertiary amines in aqueous acid.

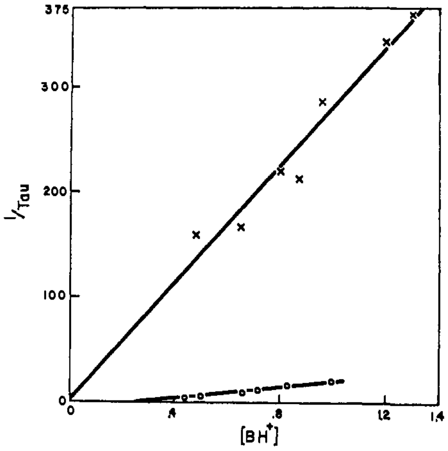

Figure 4. Concentration dependence of nitrogen inversion for DBMA and BMEA: O, DMBA at pD 2.6; ×, BMEA at pH 3.4.

$$1/\tau_i = \left(\frac{k_a k_H}{k_H + k_{-a}[H^+]}\right)\left(\frac{k_i}{k_i + k_{-H}}\right) + \frac{k_2 k_a [BH^+]}{[H^+]} \qquad (10)$$

Substitution of the kinetic parameters for proton exchange into eq 10 permits the simulation of a log $1/\tau_i$ *vs.* pH profile shown by the solid lines in Figures 1–3 for the $H_2O$ solutions. Values of $k_i/(k_i + k_{-H})$ were chosen to obtain the best fit between the experimental data and the simulated curve. Because no data other than approximated values of $k_{-H}$ are available, only the quotient is reported. The agreement between the simulated and experimental data is good.

The results presented so far were strengthened by an investigation of the inversion process in $D_2O$ solutions. The results of these studies are shown in Figures 1–3, in which the absicissa is to be read as pD. If 10 is valid, the observed rate of AB interchange for these amines in aqueous solution should be affected by solvent isotope effects in the same manner as proton exchange. The solid lines in Figures 1–3 in the case of $D_2O$ solutions represent simulated curves using eq 10, in which isotope effects upon $K_a$, $k_a$, $k_{-a}$, $k_H$, and $k_2$ were included. The isotope effect upon $K_a$ was determined by nmr and potentiometric titration.[15] The isotope effects upon $k_H$ and $k_{-a}$ were assumed to be 1.4 as predicted by Conway, *et al.*,[16] and found experimentally for trimethylamine by Day and Reilley.[17] The isotope effect upon $k_2$ was taken as 3.4 from the trimethylamine data.[17] Again the agreement between the simulated curves and experimental data is good. The isotope effect upon $K_a$ alone does not explain the difference between the data taken in $H_2O$ and $D_2O$. If eq 2 were the proper treatment for inversion in aqueous acid, the isotope effect upon $K_a$ should be sufficient.

The kinetic parameters used for the simulation of the curves shown in Figures 1–3 are given in Table II. The quotients $k_i/(k_i + k_{-H})$ used to obtain the fits to the experimental data are shown. If the value of $k_{-H}$ is taken as representing a diffusion-controlled process ($10^9$–$10^{10}$ sec$^{-1}$), the values of $k_i$ are approximately $10^8$–$10^9$ sec$^{-1}$. These values are significantly different from $10^5$ sec$^{-1}$ reported earlier for DBMA.[7] Recently, Holzman has reported inversion rate constants of $10^4$ sec$^{-1}$ for nitrogen atoms contained in five-membered ring systems and $10^6$–$10^7$ sec$^{-1}$ for those contained in

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(15) D. E. Leyden and J. M. McCall, *Anal. Chim. Acta*, **44**, 77 (1970).

(16) B. E. Conway, J. O'M. Bockris, and H. Linton, *J. Chem. Phys.*, **24**, 834 (1956).

(17) R. J. Day and C. N. Reilley, *J. Phys. Chem.*, **71**, 1588 (1967).

six-membered rings.[18] Holzman refers to the fact that inversion is found to be slower than $10^4$ sec$^{-1}$ in three- and four-membered ring systems and concludes the ease with which the nitrogen can assume a planar transition state is the dominant factor in determining the rate of inversion. Although there is some difficulty in comparing cyclic and acyclic amines, one could argue that highly substituted acyclic amines should have a more favorable planar transition state than six-membered cyclic amines.[8] Therefore, an inversion rate constant of $10^8$–$10^9$ sec$^{-1}$ for the compounds studied here is not unreasonable.

Leyden and Whidby have shown a plot of the rate of inversion of methyliminodiacetic acid *vs.* the reciprocal of the Hammett acidity function in sulfuric acid–water solvent.[19] Although the kinetics of this system are complicated by direct proton extraction by the $HSO_4^-$ ion, the shape of the plot is that predicted by eq 10 in the limit of high acidity.

The mechanism by which the second-order proton exchange process stimulates inversion is not completely understood. However, one can postulate that during this process, the salt transfers a hydronium ion to the adjacent free base in the transition complex. If the newly formed free base then inverts during the dissociation of the complex, it may be immediately hydrated (or protonated) leading to one inversion during the protolysis reaction. The possible stimulation of inversion by substituents on the amine, such as the case of ethanolamines, also requires further investigation.

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(18) L. B. Holzman, Ph.D. Dissertation, Yale University, 1968.

(19) D. E. Leyden and J. F. Whidby, *J. Phys. Chem.*, **73**, 3076 (1969).

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# Magnetic Resonance Studies of Polyradicals. II.[1] Nitronyl Nitroxide Biradicals, Nitroxide Tri- and Tetraradicals

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**Abstract:** We have examined the nmr and esr spectra of two nonconjugated nitronyl nitroxide biradicals and a tri- and tetranitroxide radical. Magnetic susceptibility measurements were made on each of these compounds. Zero-field splittings were observed from the two biradicals, and *D* and *E* values were calculated. The nmr spectra were used to determine electron–proton coupling constants. The temperature dependence of the contact shifts was monitored. These results were used to obtain estimates of the magnitudes of the exchange integrals, *J*.

The esr spectrum of a solution of a biradical with a relatively large electron–electron dipole–dipole interaction generally consists of a single broadened line.[5] When this is the case, one is unable to obtain electron–nuclei coupling constants from the esr spectrum. The spectra of solutions of biradicals with smaller dipole–dipole interactions may be well resolved, and in some cases one is able to use these spectra to estimate the magnitude of the electron–electron exchange integral ($J$).[6] Conjugated biradicals have generally been characterized by relatively large dipolar interactions, while the nonconjugated nitroxide biradicals have been observed to have smaller dipolar interactions and resolved esr spectra.

The sign and magnitude of the electron–nuclei coupling constants can be determined from the nmr spectra of the biradicals in some instances.[1] The equation relating nmr shifts ($\Delta H$) to coupling constants ($a_i$) and molar susceptibilities ($\chi_m$) is given by

$$\left(\frac{\Delta H}{H}\right) = -a_i\chi_m/Ng_n\beta_n \tag{1}$$

If the molar susceptibility of the biradical is given by[7]

$$\chi_m = \frac{S(S+1)g^2\beta^2N}{3kT}\left[\frac{1}{1 + \exp\frac{J}{RT}\exp\frac{-\Delta S}{R}}\right] \tag{2}$$

then the equation for the contact shift is

$$\left(\frac{\Delta H}{H}\right) = \frac{-a_ig\beta S(S+1)}{3kT}\left(\frac{\gamma_e}{\gamma_N}\right)\left[\frac{1}{1 + \exp\frac{J}{RT}\exp\frac{-\Delta S}{R}}\right] \tag{3}$$

In this equation, $J$ is the energy separation of the singlet and triplet states and $\Delta S$ is the entropy difference between the singlet and triplet states. If one makes independent measurements of the contact shifts and the susceptibility, one can determine the

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(1) Part I: P. W. Kopf and R. W. Kreilick, *J. Amer. Chem. Soc.*, **91**, 6569 (1969).

(2) NSF Graduate Trainee, 1966–1968; NDEA Graduate Fellow, 1968–1969; University of Rochester.

(3) Alfred P. Sloan Foundation Fellow; University of Rochester.

(4) (a) Synvar Postdoctoral Fellow, 1967–1969; (b) Contribution No. 15 from Synvar Research Institute.

(5) S. I. Weissman, *J. Chem. Phys.*, **29**, 1189 (1958).

(6) C. P. Slichter, *Phys. Rev.*, **99**, 479 (1955); D. C. Reitz and S. I. Weissman, *J. Chem. Phys.*, **33**, 700 (1960).

(7) W. D. Horrocks, *J. Amer. Chem. Soc.*, **87**, 3779 (1965).