TABLE I

PROTON MAGNETIC RESONANCE SHIFTS IN SATURATED HETEROCYCLIC COMPOUNDS

Compound	δ-Value[a]	
	α-CH_2	β-CH_2
$(CH_2)_2O$	−0.26	
$(CH_2)_3O$	− .06	−0.25
$(CH_2)_4O$	− .17	− .34
$(CH_2)_5O$	− .16	− .39
$(CH_2)S$	− .23	
$(CH_2)_3S$	− .19	− .19
$(CH_2)_4S$	− .29	− .29
$(CH_2)_5S$	− .29	− .34
$(CH_2)_2NH$	− .37	
$(CH_2)_3NH$	− .23	− .16
$(CH_2)_4NH$	− .19	− .30
$(CH_2)_5NH$	− .25	− .36

[a] The assignments of lines to the α- and β-CH_2 groups usually could be made from their relative intensities. There are some uncertainties in values for the cyclic imines because the N–H proton resonance was not always resolved from the CH_2's.

the most negative while the α-CH_2's in the 4-membered rings are among the most positive. It has been established[6] that more positive δ-values correspond to lower electron densities about the proton. Also, a low electron density on the CH_2 groups must be compensated for by a high electron density on the hetero atom. So we conclude that the hetero atom has a low electron density in the 3-membered ring and high in the 4, which agrees with the observed order of basicity.

It is also noteworthy that the changes in electron distribution with ring size appear to be more systematic at the β-CH_2 group than at the α. As the ring size increases, the δ-value for the β-CH_2 group approaches monotonically the value −0.39 observed in cyclohexane.[6]

Further study of variations in electron distribution with ring size is planned with these and other systems. More detailed data and interpretations will be presented.

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THE MECHANISM OF EXCHANGE OF HYDROGEN BETWEEN NITROGEN AND OXYGEN ATOMS

Sir:

In 1950 Brodskii and Sulima[1] reported that deuterium exchange between ammonium salts and water is slow in strongly acid solution. A very recent communication by Kaplan and Wilzbach[2] prompts us to report some results of a program we have been carrying on since 1951 in this field.

The rate of deuterium exchange between 0.3–0.5 *M* ammonium bromide and 0.1–1.2 *M* methanol in dimethylformamide solution containing 0.0013–0.13 *M* hydrogen bromide at 0° is k[salt][methanol][acid]$^{-1}$. The equilibrium constant is 1.0 since identical rates are obtained with the label in either the salt or the methanol. The half-life with 0.3 *M* salt, 0.1 *M* methanol and 0.013 *M* acid is 15 ± 2 min.

The rate usually increases with acidity of the cation or number of substituents. For example, relative rates for 0.1 *M* unsubstituted, ethyl-, diethyl-, triethyl-, trimethyl- and phenyl-ammonium chloride in methanol (0.06 *M* HCl, 0°) were 1.0:0.07:0.10:0.5:9:>100. However, guanidinium was unexpectedly >100.

There was a negative salt effect (30% decrease in k from 0.05 to 0.4 *M* $(C_2H_5)_3NH^+$, CH_3OH, 0.2 *M* HCl).

The rate usually decreases with increasing polarity of the solvent. Toluene (0.1 *M* methanol) was immeasurably fast, ethanol was faster than methanol, and ethylene glycol was slow (half-life of one hour). However, acetic and formic acid were immeasurably fast and addition of 0.1 *M* water increased the rate for 0.9 *M* triethylammonium chloride (CH_3OH, 0.4 *M* HCl, 0°) from 2 to 8×10^{-4} *M* sec.$^{-1}$. At 25° this rate (without water) was 5×10^{-3} *M* sec.$^{-1}$, and was unchanged by replacing all chloride by p-toluenesulfonate.

Tritium exchange with 0.2 *M* triethylammonium chloride (CH_3OH, 0.2 *M* HCl, 0°) was 0.8 as fast as deuterium exchange.

The proposed[3,4] mechanism is

$$R_3NH^+ + ROD + \text{Solvent} \underset{k_3}{\overset{k_2}{\rightleftarrows}} R_3N\cdot\cdot H\cdot\cdot OR + \text{Solvent } D^+$$

$$R_3N\cdot\cdot H\cdot\cdot OR \underset{k_5}{\overset{k_4}{\rightleftarrows}} R_3N + ROH$$

and reversal through similar steps to R_3ND^+, with k_3 [Solvent D^+] > k_4. The hydrogen-bonded complex may be between amine and alcohol (transition state in first step) or between ammonium and alkoxide ions (transition state in second step). The mechanism

$$R_3NH^+ + RO^- \rightleftarrows R_3N + ROH$$

is excluded for the exchange with ethanol at least, because the calculated ratio $[C_2H_5O^-]$/[transition state] is 10^{-5}. The mechanism

$$NH_4^+ + \text{Solvent} \rightleftarrows NH_3 + \text{Solvent } H^+$$

$$NH_3 + ROD \rightleftarrows NH_2D + ROH$$

is possible for some cations but not for a tertiary ammonium ion.

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(1) A. I. Brodskii and L. V. Sulima, *Doklady Akad. Nauk. S.S.S.R.*, **74**, 513 (1950).

(2) Kaplan and Wilzbach THIS JOURNAL, **76**, 2593 (1954).

(3) J. T. McKnight, Ph.D. thesis, M.I.T., September, 1953; M. M. Labes, Ph.D. thesis, M.I.T., February, 1954.

(4) M.I.T. Laboratory for Nuclear Science Progress Reports, August 31 and November 30, 1953, and February 28, 1954.