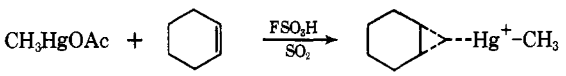
It has also been possible to obtain the cyclohexylenemethylmercurinium ion **6** by the direct mercuration of cyclohexene. Methylmercuric acetate dissolves in FSO_3H-SO_2 to give CH_3Hg^+ (**7**) ($\delta_{CH_3} = 1.58$, $J_{^{199}Hg-CH_3} = 246$ Hz)[3,4] and protonated acetic acid. If equimolar mixtures of CH_3HgOAc in FSO_3H-SO_2 and cyclohexene in SO_2 are mixed, ion **6** is formed. The pmr spectrum of ion **6** at −90° is quite analogous to that of ion **2** consisting of a singlet at δ 7.27 (2 H, $J_{^{199}Hg-H} =$ 54 Hz), a multiplet at 2.65 (4 H), a multiplet at 1.86 (4 H), and a singlet at 1.46 (3 H). In addition, singlets at 2.86 (due to protonated acetic acid) and 1.54 (due to excess CH_3Hg^+) may be observed.[5]



6

When a solution of ion **6** prepared in this manner is progressively warmed to −60°, the singlets at δ 1.54 and 1.46 merge into a single line while the peaks due to the ring protons of ion **6** broaden slightly. These observations are consistent with the equilibrium process shown below. If such a process were occurring, one would expect to see a considerable broadening of the mercury–proton satellites due to the exchange of cyclohexene between $CH_3{}^{199}Hg^+$[6] and $CH_3{}^{200}Hg^+$ or $CH_3{}^{201}Hg^+$. In fact, at −60° the mercury–proton satellites have broadened to the point of virtual disappearance.

The same equilibrium process may be observed for ion **6** at other concentrations of cyclohexene and methylmercuric acetate. However, there are no spectral indications for the occurrence of such a process for either ion **2** or for any of the other ions studied.

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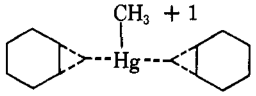
[3] CH_3HgClO_4 in water is thought to be $CH_3HgOH_2{}^+$ and has $J_{^{199}HCH} = 259$ Hz.[4] Thus, CH_3HgOAc in FSO_3H may well be CH_3HgOSO_2F. However, for simplicity the designation CH_3Hg^+ will be used. CH_3Hg^+ may well be generated from CH_3HgCl and SbF_5 in SO_2 or SO_2ClF. In these solvents, the coupling constants are $J_{^{199}HgCH} = 312$ Hz and $J_{^{199}HgCH} = 328$ Hz, respectively.

[4] J. V. Hatton and W. O. Schneider, *J. Chem. Phys.*, **39**, 1330 (1963).

[5] We have attempted to determine if **6** is actually the 1:1 complex indicated or is better represented as the 2:1 complex **6′** by a study of the stoichiometry of ion formation. In the solvent system used such determinations are extremely difficult and no conclusive results were so far obtained.



6′

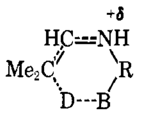
[6] The natural abundance of ^{199}Hg is 16.86%.

[7] National Institutes of Health Postdoctoral Research Fellow, 1969–1970.

Bifunctional Catalysis of the Dedeuteration of Acetone-d_6 by 3-Dimethylaminopropylamine and 2-(Dimethylaminomethyl)cyclopentylamines[1]

Sir:

Species of the type $B-R-NH_2$ may catalyze the dedeuteration of isobutyraldehyde-*2-d* bifunctionally; the amino group may transform the aldehyde to an imine, which is in equilibrium with the corresponding iminium ion, and the basic group B may then remove the deuterium internally *via* a transition state such as **1**.



1

No evidence for bifunctional catalysis was found with amino acids of the type $^+H_3N(CH_2)_nCO_2{}^-$, where n was 1–5, as catalysts,[1c] but bifunctional catalysis was found with polyethylenimines.[2] This difference in behavior was attributed to the largely trans stereochemistry of the intermediate iminium ion. The amino acids used are not long enough for the basic carboxylate anion group to reach the deuterium atom when the iminium ion is trans, but the much higher molecular weight polyethylenimines are.

We have now studied diamines of the type $Me_2N(CH_2)_nNH_2$, where n is 2–5, as catalysts for the dedeuteration of isobutyraldehyde-*2-d* and of acetone-d_6 (which undergoes enzymatic dedeuteration *via* an iminium ion[3]), in which the problem of cis–trans isomerism of the iminium ion is avoided. The results of runs made at pH's where the concentration of the monoprotonated form of the diamine is a maximum (so that the rate of the bifunctionally catalyzed reaction will be a maximum if deuterium removal is rate controlling) are summarized in Figure 1. The first-order rate constants for the dedeuteration of ~0.1 M isobutyraldehyde-*2-d* were obtained as described previously[4] in the presence of ~0.13 M total diamine, and those for the transformation of 0.5 M acetone-d_6 to less deuterated species were obtained by a mass spectral method[5] in the presence of ~0.05 M total diamine. Corrected apparent second-order rate constants, obtained by subtracting that part of the reaction due to hydroxide ions (less than 3%) and then dividing the first-order rate constants by the total diamine concentrations, are plotted logarithmically against the acidity constants of the diprotonated diamines. If the monoprotonated diamines are acting as simple basic catalysts such a Brønsted plot should approximate a straight line, but if bifunctional catalysis is occurring, a maximum might appear where the cyclic transition state has the optimum ring size. The ability of the monoprotonated diamines to catalyze the dedeuteration of isobutyraldehyde-*2-d* is seen to increase mono-

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[1] (a) This investigation was supported in part by Public Health Service Research Grants AM 06829-MCB and AM 10378; (b) Catalysis of α-Hydrogen Exchange. X. For Part IX see: (c) J. Hine, B. C. Menon, J. Mulders, and R. L. Flachskam, Jr., *J. Org. Chem.*, **34**, 4083 (1969).

[2] J. Hine, F. E. Rogers, and R. E. Notari, *J. Amer. Chem. Soc.*, **90**, 3279 (1968).

[3] W. Tagaki and F. H. Westheimer, *Biochemistry*, **7**, 901 (1968).

[4] *Cf.* J. Hine, J. G. Houston, J. H. Jensen, and J. Mulders, *J. Amer. Chem. Soc.*, **87**, 5050 (1965).

[5] J. C. Kaufmann, M.S. Thesis, The Ohio State University, 1969.

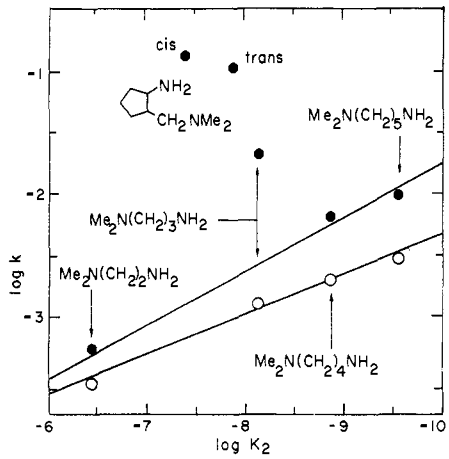
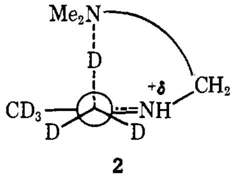


Figure 1. Brønsted plot for the dedeuteration of isobutyraldehyde-*2-d* (open symbols) and acetone-d_6 (solid symbols). K_2 is the acidity constant for the loss of one proton from the diprotonated diamine and k is the apparent second-order rate constant (in M^{-1} sec^{-1}) for catalysis by the monoprotonated diamine in water at 35°.

tonically with the basicity of the catalyst, but in the case of acetone-d_6, 3-dimethylaminopropylamine is seen to be about seven times as reactive as would be expected from the results obtained with the other ω-dimethylaminoalkylamines, whose points approximate a line roughly parallel to the one described by the points for the dedeuteration of isobutyraldehyde-*2-d*. Further observations, that the reaction in the presence of 3-dimethylaminopropylamine at a given pH is first order in amine and that a marked rate maximum in a pH-rate plot is found for 3-dimethylaminopropylamine but not for the other three ω-dimethylaminoalkylamines, add to the evidence that the monoprotonated form of 3-dimethylaminopropylamine is a bifunctional catalyst for the dedeuteration of acetone-d_6, whereas the other monoprotonated ω-dimethylaminoalkylamines are much poorer bifunctional catalysts, at best.

It therefore appears that in this series the optimum cyclic transition state contains an eight-membered ring,[6] a fact most reasonably interpreted in terms of stereoelectronic effects. Since the carbon-deuterium bond being broken should be in a plane nearly perpendicular to the plane of the iminium double bond[4] and since the C-D-N grouping should preferentially be linear,[7] the cyclic transition state should have a structure like that shown in Newman projection **2**. Molecular models show that although four carbon



2

atoms between the two nitrogen atoms of the catalyst are required to construct **2** with a linear C-D-N grouping, C-D-N angles of about 150° can be obtained with only three carbon atoms between the two nitrogens. Apparently, the advantage that 4-dimethylaminobutylamine may derive from having a linear C-D-N grouping in its transition state is more than offset by the disadvantages of having a longer polymethylene chain between the two functional groups.

In the case of 3-dimethylaminopropylamine each of the two plausible models of the transition state has carbon atoms 1 and 2 eclipsed. As seen in Figure 1, the 2-(dimethylaminomethyl)cyclopentylamines, in which such eclipsing is more or less frozen into the molecule, are considerably better catalysts than any of the acyclic diamines studied. The cis isomer is about 100 times as active as would be expected from the best straight line through the three points for ω-dimethylaminoalkylamines that were not shown to be bifunctional catalysts.

With each of the three bifunctional catalysts the dedeuteration of acetone-d_6 gave acetone-d_5, -d_4, and -d_3 (but not -d_2, -d_1, or -d_0) directly from the beginning of the reaction, whereas with the other catalysts the less deuterated species were formed consecutively with no appreciable amount of d_3, for example, being formed until much larger amounts of d_4 had been formed. This shows that the iminium ions formed from the bifunctional catalysts lose deuterium (from the trideuteriomethyl group cis to the ω-dimethylaminoalkyl group) and hydrolyze to acetone at comparable rates.

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(8) Public Health Service Postdoctoral Fellow, 1969–1971.

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Beryllium Borohydride Structure in the Solid Phase

Sir:

Both bent[1-4] and linear[5,6] structures for BBeB in $Be(BH_4)_2$ have been suggested, with a variety of arrangements for bonds toward hydrogen atoms. Indirect evidence from the crystallographic diffraction pattern led to the conclusion[7] that the solid phase consisted of discrete molecules. Our solution of this structure from a single crystal establishes that the solid consists of helical polymers, having a chemical repeat shown in Figure 1 and a crystallographic polymeric unit shown in Figure 2.

In agreement with the earlier study[7] the space group is $I4_1cd$. Cell parameters are $a = 13.62 \pm 0.01$ and $c = 9.10 \pm 0.01$ Å, and the assumption of 16 formula weights in the unit cell gives a reasonable calculated density of 0.609 g cm^{-3}. The structure was solved from its symmetry minimum function[8,9] and its Patterson function. Some 276 diffraction maxima, measured at 5° with the use of Cu Kα radiation and a Picker automated diffractometer, have yielded a value of R (de-

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(3) T. H. Cook and G. L. Morgan, *J. Amer. Chem. Soc.*, **91**, 774 (1969).

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(9) P. G. Simpson, R. D. Dobrott, and W. N. Lipscomb, *Acta Crystallogr.*, **18**, 169 (1965).