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Micellar Control of the Nitrous Acid Deamination Reaction. A Unique Salt Effect on Stereochemistry

Sir:

In contrast to micellar effects on reaction rates,[1] little is known about micellar control of stereochemistry. We discovered micellar alteration of the stereochemistry of alcohol formation in the deamination of amines.[2] Others have reported stereoselective hydrolyses of chiral esters catalyzed by chiral micelles,[3] and micellar enhancement of the mutarotation of 2,3,4,-6-tetramethyl-α-D-glucose.[4]

Now, we demonstrate that stereochemical modification of the deamination reaction *requires both alkylammonium micelles and certain relatively hydrophobic counterions*. Moreover, whereas the counterion identity is crucial to the product-forming step, which determines stereochemistry, micellar catalysis of the rate-determining nitrosation step[5] displays only a mild dependence on counterion.

l-2-Aminooctane was deaminated at various concentrations in 1.59 *M* aqueous $NaNO_2$, at pH 4, adjusted with $HClO_4$ or HCl.[6,7] The reaction stereochemistry was determined[8] (to $\pm 1\%$) from the optical purities of the gc-isolated product 2-octanol and the initial 2-aminooctane. We also determined pseudo-first-order rate constants (k_{obsd}) for these deaminations.[9]

Twenty-five experiments are represented in Figure 1, which relates the reaction stereochemistry and k_{obsd} to F_m, the fraction of the initial 2-octylammonium ions which are micellized.[10] Mechanistically, each perchlorate stereochemical result is the "weighted average" of a micellar deamination and a much slower nonmicellar deamination. This function is only approximately linear in F_m, but can be calculated within 2% by treating the reaction as the sum of a micellar fraction (F_m),[10] with characteristic stereochemistry of 6% net retention, and a nonmicellar fraction ($1 - F_m$), with characteristic stereochemistry of 24% net inversion.

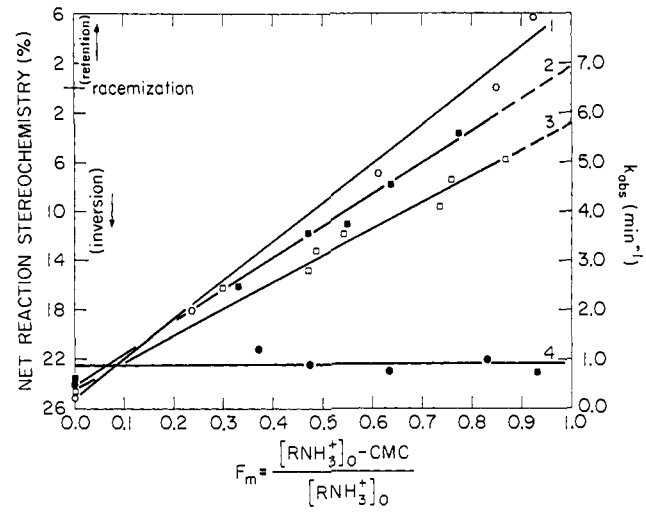

Figure 1. The stereochemistry and kinetics of the nitrous acid deamination of 2-aminooctane: curve 1, stereochemistry, perchlorate counterions; curve 2, kinetics, chloride counterions; curve 3, kinetics, perchlorate counterions; curve 4, stereochemistry, chloride counterions. The rate constants, as shown on the right-hand ordinate, have been arbitrarily multiplied by 10.0.

Clearly, deamination reactions are accelerated by 2-octylammonium micelles whatever the counterion, but the stereochemistry of 2-octanol formation is altered only when micelles are present *and* perchlorate is the counterion. The following experiments highlight the need for both micelles and specific anions in order to control stereochemistry.[12]

(a) Solutions containing excess 2-decylammonium and low concentrations of 2-octylammonium ions were deaminated, affording 2-octanol with up to 5.4% net retention. In these experiments, 2-decylammonium micelles provided a template for 2-aminooctane deamination, which therefore occurred with a stereochemistry characteristic of $F_m > 0.9$. However, perchlorate was necessary; parallel experiments with chloride counterions gave 2-octanol with 21–22% ("normal") net inversion.

(b) Inclusion of $NaClO_4$ in $NaNO_2$–HCl deaminations shifted the stereochemistry toward increased retention. Added perchlorate did not affect $NaNO_2$–$HClO_4$ deaminations.

(c) Deaminations ($[RNH_3^+]_0$ > cmc) which used $NaNO_2$–HBr, or which occurred in excess (micellar) 2-octyltrimethylammonium bromide solutions, *did not* afford 2-octanol with enhanced retention, although k_{obsd} was augmented.

(d) Fluoroborate and *p*-tosylate resembled perchlorate in eliciting stereochemical micellar control. At $F_m \sim 0.8$, $NaNO_2$–HBF_4 and $NaNO_2$–*p*-$CH_3C_6H_4SO_3H$ deaminations gave 2-octanol with 15 and 7% net inversion, respectively. At $F_m \leq 0$, 23% net inversion was observed in each case.

The rate of nitrosation of *free* amine by N_2O_3 determines the rate of deamination[13] and k_{obsd} can be shown

(1) Reviews include: E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970); E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, 2, 329 (1969); and H. Morawetz, *Advan. Catal.*, 20, 341 (1969).

(2) R. A. Moss and D. W. Reger, *J. Amer. Chem. Soc.*, **91**, 7539 (1969).

(3) C. A. Bunton, L. Robinson, and M. F. Stam, *Tetrahedron Lett.*, 121 (1971). See also, C. A. Bunton, L. Robinson, and M. F. Stam, *J. Amer. Chem. Soc.*, **92**, 7393 (1970).

(4) E. J. Fendler, J. H. Fendler, R. T. Medary, and V. A. Woods, *Chem. Commun.*, 1497 (1971).

(5) R. A. Moss and C. J. Talkowski, *Tetrahedron Lett.*, 703 (1971).

(6) Protonation of the amine exceeds 99% under these conditions; 2-octylammonium perchlorate or chloride is the 2-aminooctane "reservoir."

(7) General deamination procedures appear in ref 2, and in R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, **89**, 5655 (1967).

(8) R. A. Moss, D. W. Reger, and E. M. Emery, *ibid.*, **92**, 1366 (1970).

(9) Methodological details appear in ref 5.

(10) $F_m = ([RNH_3^+]_0 - \text{cmc})/[RNH_3^+]_0$, where 0 denotes initial concentration, and cmc the critical micelle concentration for RNH_3^+ under simulated reaction conditions. Details of the cmc determinations[11] are available on request, and will be published in full. The dependence of 2-octylammonium cmc on $[RNH_3^+]_0$ (0.08–0.6 *M*) was small. Best values, used to calculate F_m, were 0.058 (perchlorate counterions) and 0.09 *M* (chloride counterions).

(11) Related determinations appear in R. A. Moss and W. L. Sunshine, *J. Org. Chem.*, **35**, 3581 (1970).

(12) Details will appear in the full paper.

(13) J. H. Ridd, *Quart. Rev., Chem. Soc.*, **15**, 418 (1961); T. W. J. Taylor, *J. Chem. Soc.*, 1099 (1928); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, p 294; and J. H. Dusenbury and R. E. Powell, *J. Amer. Chem. Soc.*, 73, 3266 (1951).

to include $K_a^{RNH_3^+}$, which is exalted upon micellization.[5,14] Moreover, $[NO_2^-]$ will be abnormally high near the micelles. Both effects enhance k_{obsd}, which approaches 0.7 (chloride) and 0.6 min^{-1} (perchlorate) as F_m approaches 1.0. Because the catalysis is electrostatic in origin and depends on the cationic character of the micelles, only a minor dependence on counterion identity is observed.

The stereochemistry of 2-octanol formation depends on partition of 2-Oct—N=N—OH between nitrogen loss with (a) return of OH (retention), (b) displacement by water (inversion), and (c) escape to hydrated 2-octyl cations (racemization).[15] In water, or in highly aqueous Stern layers of alkylammonium micelles which are relatively *weakly* associated[16] with their counterions (*e.g.*, bromide, chloride, and nitrite, which have high hydration energies[17]), the partition's resultant is ~24% net inversion. But counterions which are poorly hydrated[17] and therefore *strongly* bound to the micelles[16,18] (perchlorate, fluoroborate, and *p*-tosylate) engender larger, more effectively charge-neutralized, and (probably) denser, less hydrated micelles.[16] In such "less aqueous" environments, partition process a is enhanced relative to b and c; the resultant moves toward retention.[19]

The new stereochemical salt effects differ intriguingly from the more commonly observed competitive inhibition by foreign ions of micelle-catalyzed reactions, which typically involves the exclusion, by counterion A, of reactant counterion B from the micelle which solubilizes the substrate.[20] In the present work, it seems very likely that the micelles themselves have been altered through strong binding of certain counterions, which, though not incorporated into product, modify product formation occurring within the Stern layers of which they are a part. Similar mechanisms may underlie recently observed phenomena in the micelle-catalyzed decarboxylation of the 6-nitrobenzisoxazole-3-carboxylate ion.[21]

We are continuing our studies of these and related reactions, searching for new and more stereospecific examples of micellar control of reaction stereochemistry.

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(14) M. T. Behme and E. H. Cordes, *J. Amer. Chem. Soc.*, **87**, 260 (1965), report an analogous effect.

(15) For analyses of this partition under basic conditions, see ref 8, and R. A. Moss, A. W. Fritz, and E. M. Emery, *J. Org. Chem.*, **36**, 3881 (1971).

(16) E. W. Anacker and H. M. Ghose, *J. Phys. Chem.*, **67**, 1713 (1963); R. D. Geer, E. H. Eylar, and E. W. Anacker, *ibid.*, **75**, 369 (1971); E. W. Anacker and R. D. Geer, *J. Colloid Interface Sci.*, **35**, 441 (1971), and references cited therein.

(17) H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, **59**, 1126 (1963); *J. Chem. Soc.*, 4603 (1960); S. Subramanian and H. F. Fisher, *J. Phys. Chem.*, **76**, 84 (1972).

(18) K. J. Mysels, "Study of the Properties of Micelles," Final Report to the Office of Naval Research, Project NR 356-254, Nov 1961, pp 13–14.

(19) Discussions of medium effects on deamination stereochemistry appear in E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, p 440ff, and R. A. Moss, *Chem. Eng. News*, **49** (48), 28 (November 22, 1971).

(20) Examples include: R. B. Dunlap and E. H. Cordes, *J. Amer. Chem. Soc.*, **90**, 4395 (1968); L. R. Romstead and E. H. Cordes, *ibid.*, **90**, 4404 (1968); C. A. Bunton and L. Robinson, *J. Org. Chem.*, **34**, 773, 780 (1969). Other examples are cited in ref 1.

(21) C. A. Bunton, M. Minch, and L. Sepulveda, *J. Phys. Chem.*, **75**, 2708 (1971).

(22) Alfred P. Sloan Foundation Fellow; National Institutes of Health Special Postdoctoral Fellow.

(23) Johnson and Johnson Fellow.

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Synthesis and Rearrangement of μ,μ'-$SiH_2(C_2B_4H_7)_2$, a Bis(carboranyl)silane Linked by a Silicon Atom Common to Two Three-Center Boron–Silicon–Boron Bonds

Sir:

The preparation and chemistry of heteroatom-bridged small carboranes of the type μ-$MR_3C_2B_4H_7$, in which M is silicon,[1] germanium,[1] tin,[2] or lead,[2] and R is hydrogen or an alkyl group, have been of recent interest in our laboratory. In each case the M atom occupies a bridging position on the edge of a pentagonal pyramidal $C_2B_4H_7$ cage, formally replacing one of the two bridge hydrogens in parent $C_2B_4H_8$.[3] The bridging heteroatom is considered to utilize approximately sp^3 tetrahedral orbitals, three of which are involved in bonding to the R ligands while the remaining orbital combines with orbitals from the adjacent borons to form a three-center two-electron B–M–B bond.[4]

Extension of this structural principle to a bis(μ-carboranyl)silane, in which two of the sp^3 orbitals on silicon participate in separate three-center bridge bonds, seemed possible in theory, although no such borane or carborane species has been described. We now report the synthesis of μ,μ'-silylenebis(2,3-dicarba-*nido*-hexaboranyl) (I) from the reaction of dichlorosilane with sodium dicarbahexaborate(1−) in tetrahydrofuran at 0°.

$$SiH_2Cl_2 + 2Na^+C_2B_4H_7^- \longrightarrow \mu,\mu'\text{-}SiH_2(C_2B_4H_7)_2 + 2NaCl$$

Compound I is obtained in 70% yield as a viscous, colorless liquid of low volatility. The mass spectrum exhibits a cutoff at *m/e* 181 corresponding to the $^{29}Si^{12}C_4{}^{11}B_8{}^1H_{16}^+$ parent ion, and the profile in the parent region is consistent with the indicated composition. The significant infrared bands are at 3020 (w) (C–H), 2590 (s) and 2530 (s) (B–H), and 2150 cm^{-1} (s) (Si–H). The 32.1-MHz ^{11}B nmr spectrum (Figure 1a) contains four doublets of equal area corresponding to four pairs of magnetically equivalent B–H groups, thus establishing that no B–Si terminal bonds are present. The doublet assigned to B(6,6′)–H is further split due to the adjacent bridge proton; in contrast, B(5,5′) is more directly affected by silicon than is B(6,6′) and fails to

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(2) A. Tabereaux and R. N. Grimes, manuscript in preparation.

(3) Closely related derivatives of C,C′-$(CH_3)_2C_2B_4H_6$ containing bridging trimethylsilyl and trimethylgermyl groups have also been reported: C. H. Savory and M. G. H. Wallbridge, *Chem. Commun.*, 622 (1971).

(4) Direct crystallographic evidence for the existence of three-center B–Si–B bonds in the related species μ-$(CH_3)_3SiB_5H_8$ has been obtained in an X-ray diffraction study of the 1-bromo derivative: J. C. Calabrese and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 6042 (1971).