Micellar Control of Stereochemistry and Kinetics in the Nitrous Acid Deamination Reaction[1]

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Abstract: Critical micelle concentrations were determined for 2-octylammonium and 2-octyltrimethylammonium ions in the presence of various counterions. The kinetics and the stereochemistry of the aqueous nitrous acid deamination of 2-aminooctane were studied under micellar and nonmicellar conditions. Micellar catalysis of the deaminative rate (about 15-fold) was observed. Some catalysis was observed, whatever the identity of the anions present during the deamination. The stereochemistry of the 2-aminooctane to 2-octanol conversion could be changed from 24% net inversion (nonmicellar) to 6% net retention, under certain micellar deamination conditions. In contrast to the kinetic results, the stereochemical effects were highly dependent on the identity of the counterions. No stereochemical changes were seen in micellar deaminations conducted in the presence of chloride, bromide, or acetate counterions. Perchlorate, fluoroborate, *p*-tosylate, or *d*-10-camphorsulfonate counterions were required for micellar stereochemical control of deamination. Interpretive discussions are presented.

Since its discovery, more than a century ago,[3] the nitrous acid deamination reaction has been intensively studied.[4] The reaction mechanism has been of primary concern, particularly in regard to the nature of the cationic intermediates.[4] Our interest in the generation of diazonium intermediates by the basic hydrolysis of alkane diazotates[5] also caused us to investigate the stereochemistry of the nitrous acid deamination of simple 2-aminoalkanes.

In the course of the initial experiments, Lane[6] observed that 2-aminooctane deaminated much more rapidly than 2-aminobutane under comparable conditions, and that, whereas the latter afforded 2-butanol with the ~20% net inversion anticipated,[7] the 2-aminooctane appeared to give *rac*-2-octanol. That micellar phenomena were responsible for these unexpected results was strongly confirmed by subsequent experiments,[8-10] which included the first demonstrations[8] of micellar alteration of stereochemistry in a simple organic reaction.[11] In the present full paper, we provide details of the previous work, new results, and interpretive discussions.

Results and Discussion

Critical Micelle Concentrations. The determination of the critical micelle concentration (cmc) of an alkylammonium ion under deamination conditions proved essential to our mechanistic studies. In a typical deamination reaction, nitrous acid is generated *in situ* by acidification of aqueous sodium nitrite with a mineral acid, HX. The reaction medium thus contains nitrite and X anions. The cmc's of cationic surfactants, such as alkylammonium ions, depend strongly on the *concentrations* and *identities* of all anions which are present.[12] However, a deamination solution rapidly evolves nitrogen as the alkylammonium ions it contains are destroyed through deamination of the corresponding amine, and the cmc's of such solutions cannot be directly determined.

We required a model system which simulated deamination conditions, but in which cmc's could be measured. Specifically, we sought an *inert* anion which, in its influence on surfactant cmc's, closely resembled nitrite. The model anion could then be used in the preparation of alkylammonium ion solutions which were analogous to the deamination solutions.

2-Octyltrimethylammonium bromide (2-OTA-Br) was prepared from 2-aminooctane,[13] and converted to 2-OTA-X (X = Cl, NO_2, and NO_3) by ion exchange

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(2) (a) Fellow of the A. P. Sloan Foundation. (b) Johnson and Johnson Fellow; much of this work is taken from the Ph.D. Thesis of C. J. Talkowski, Rutgers University, 1973. (c) Allied Chemical Co. Fellow.

(3) R. Piria, *Justus Liebigs Ann. Chem.*, **68**, 343 (1848).

(4) Reviews include: (a) R. A. Moss, *Chem. Eng. News*, **49** (48), 28 (November 22, 1971); (b) L. Friedman in "Carbonium Ions," II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 655 ff; (c) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, p 440 ff; (d) M. C. Whiting, *Chem. Brit.*, **2**, 482 (1966); (e) J. H. Ridd, *Quart. Rev., Chem. Soc.*, **15**, 418 (1961); (f) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961; (g) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

(5) (a) R. A. Moss, D. W. Reger, and E. M. Emery, *J. Amer. Chem. Soc.*, **92**, 1366 (1970); (b) R. A. Moss, A. W. Fritz, and E. M. Emery, *J. Org. Chem.*, **36**, 3881 (1971).

(6) R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, **89**, 5655 (1967); S. M. Lane, Ph.D. Thesis, Rutgers University, 1968.

(7) P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold, and P. A. D. S. Rao, *Nature (London)*, **166**, 179 (1950).

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

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

(10) R. A. Moss and C. J. Talkowski, *J. Amer. Chem. Soc.*, **94**, 4767 (1972).

(11) Reviews of micellar organic chemistry include: (a) E. H. Cordes and C. Gitler, *Progr. Bioorg. Chem.*, **2**, E. T. Kaiser and F. J. Kézdy, Ed., in press; (b) E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970); (c) H. Morawetz, *Advan. Catal. Relat. Sub.*, **20**, 341 (1969); (d) E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 329 (1969). (e) An excellent annotated bibliography is given by R. H. Prince, Ed., *Chem. Ind. (London)*, 596 (1971).

(12) (a) P. H. Elworthy, A. T. Florence, and C. B. Macfarlane, "Solubilization by Surface-Active Agents," Chapman and Hall, London, 1968; (b) P. Mukerjee, *Advan. Colloid Interface Sci.*, 1, 241 (1967); (c) K. Shinoda, T. Nakagawa, B.-I. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York, N. Y., 1963. Further discussion and specific references will appear below.

(13) R. A. Moss and W. L. Sunshine, *J. Org. Chem.*, **35**, 3581 (1970).

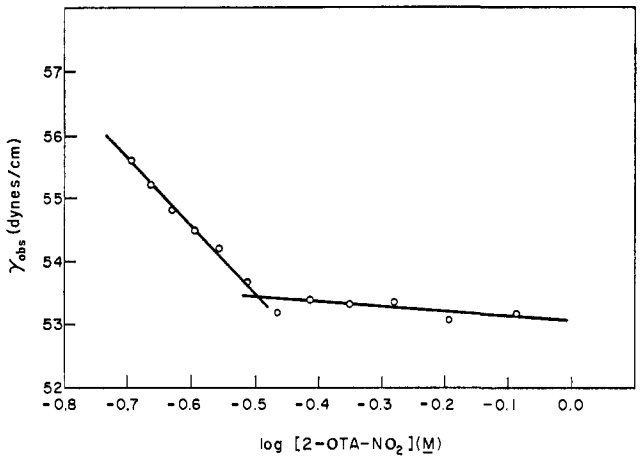


Figure 1. The observed surface tension (γ) of 2-OTA-NO_2 in 0.5 *M* aqueous $NaNO_2$ *vs.* log [2-OTA-NO_2]. The break-point occurs at log [2-OTA-NO_2] = −0.497; the cmc is 0.318 *M*.

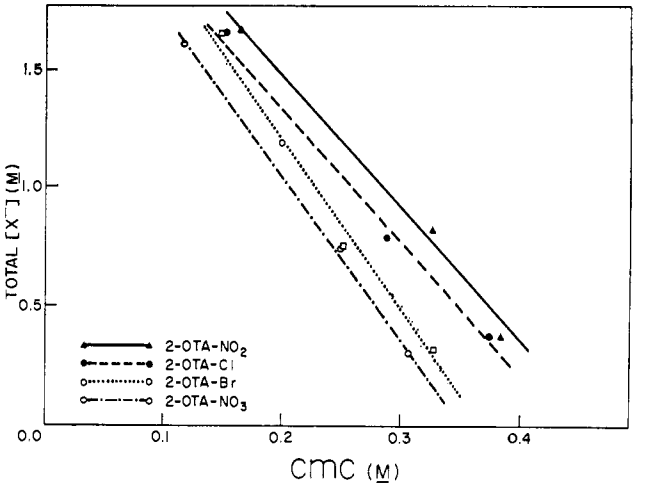


Figure 2. Total anion concentration, [X^-], *vs.* the experimentally determined cmc's of 2-OTA-X.

chromatography on Dowex 21K, type 1 resin. The cmc's of 2-OTA-X were determined at various background [NaX], using the surface tension method.[14] A representative determination is shown in Figure 1,[15] and the data collected in this manner are summarized in Table I.

Table I. Anion and Concentration Dependence of Cmc Values

2-OTA-X	Cmc, *M*[a]		[NaX], *M*
2-OTA-NO_2	0.305 (±)	0.002	0.0
	0.249	0.014	0.5
	0.116	0.005	1.5
2-OTA-Br	0.325	0.022	0.0[b]
	0.249	0.009	0.5
	0.195	0.003	1.0
	0.148	0.004	1.5[b]
2-OTA-Cl	0.373	0.004	0.0
	0.286	0.012	0.5
	0.151	0.007	1.5
2-OTA-NO_2	0.383	0.003	0.0
	0.326	0.002	0.5
	0.164	0.002	1.5

[a] These values are means of two determinations. [b] From ref 13.

From Table I, we constructed Figure 2, in which the cmc of 2-OTA-X was plotted against total [X^-]. It is apparent that the behavior of 2-OTA-Cl is closest to that of 2-OTA-NO_2, and chloride was therefore chosen as a model for nitrite.

The similarity of chloride and nitrite ions is not surprising, for they are nearest neighbors in the lyotropic series,[16] which correlates such phenomena as the binding of anions to ion exchange resins,[17] and their abilities to depress the cmc of alkylammonium ions.[18]

Model deamination systems were prepared. These contained 2-aminooctane at concentration C_i, 1.6 *M* NaCl (representing $NaNO_2$), and sufficient mineral acid, HX, to adjust the systemic pH to 4.0.[19a] The cmc's of the model systems were determined by the surface tension method,[14] employing titrants which contained 1.6 *M* NaCl, NaX at concentration C_i, and a few drops of HX (to pH 4).

Cmc's determined in this way are somewhat dependent on the particular choice of C_i, for this also determines [X^-], but the dependence is not very large, as the data in Table II demonstrate.

Table II. Cmc's of 2-Octylammonium Ion under "Deamination Conditions"[a]

C_i of 2-C_8H_{17}-NH_3^+	[HX], *M*[b]	Titrant, *M*	Cmc, *M*[c]
0.603	$HClO_4$, 0.60	$NaClO_4$, 0.60 NaCl, 1.6	0.054 ± 0.001
0.103	$HClO_4$, 0.10[d]	$NaClO_4$, 0.23 NaCl, 1.6	0.058
0.162	$HClO_4$, 0.16	$NaClO_4$, 0.16 NaCl, 1.6	0.060 ± 0.002
0.803	HCl, 0.80	NaCl, 2.4[e]	0.082 ± 0.009
0.205	HCl, 0.20	NaCl, 1.8[e]	0.078 ± 0.001

[a] In 1.6 *M* NaCl, simulating 1.6 *M* $NaNO_2$. [b] Added to the solution until pH 4. [c] Average of two trials, except for the second entry. [d] 0.13 *M* "excess" $NaClO_4$ was added to simulate $HClO_4$ introduced due to protonation of nitrite. [e] Sum of chloride in sample solution (1.6 *M*) and that introduced by the added HCl.

Later in our studies, it became necessary to know how other counterions affected the cm's of 2-octylammonium ion under deamination conditions. Model techniques were utilized in these new cmc determinations. Table III gathers all of the cmc values we have determined. Only the Cl^- and ClO_4^- values were determined at several 2-octylammonium ion concentrations; the other values should be considered approximate.

(14) See the Experimental Section, and ref 13.
(15) Further examples appear in the Ph.D. Thesis of C. J. T.[2b]
(16) A. Voet, *Chem. Rev.*, **20**, 169 (1937).
(17) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, p 359 ff.
(18) E. W. Anacker and H. M. Ghose, *J. Phys. Chem.*, **67**, 1713 (1963), and references therein.

(19) (a) The *standard* deamination conditions were 2-aminoalkane at concentrations up to 0.8 *M*, 1.59–1.61 *M* $NaNO_2$, and HX added until pH 4. At pH 4, 2-aminoalkanes are more than 99% protonated, and the concentration of 2-alkylammonium ion is essentially that of the initial 2-aminoalkane. The concentration of X^- is therefore *at least* C_i. In reality, some HX is used to protonate NO_2^-, and, at pH 4, [X^-] will exceed C_i. We estimate that 1.6 *M* $NaNO_2$ will generate ~0.19 *M* ClO_4^-, when adjusted to pH 4, with $HClO_4$.[19b] (b) See the Appendix of ref 2b for the method of estimation.

Table III. Cmc's of 2-Octylammonium Ion[a]

Anion	Cmc, M[b]
Cl^-	0.090[c]
CH_3COO^-	0.089 ± 0.004
BF_4^-	0.076 ± 0.002
Br^-	0.074 ± 0.006
ClO_4^-	0.058[d]
d-10-Camphorsulfonate	0.045 ± 0.003
p-Toluenesulfonate	0.029 ± 0.003[e]

[a] In 1.6 M NaCl, 25°, pH 4. [b] Average of two trials, unless otherwise indicated. [c] 0.01 has been added to the average value of Table II to account for the difference in cmc-lowering ability of Cl^- and NO_2^-, as shown in Figure 2. [d] From Table II. [e] At 34°.

Kinetics. The rate-determining step in the deamination sequence is the *nitrosation of free amine.*[4] The subject has been reviewed by Ridd,[4e] and there is now general agreement that, in moderately acidic aqueous acid, the reaction is first order in amine and second order in nitrite. The latter dependence reflects the fact that the actual nitrosating agent is nitrous anhydride (N_2O_3), not nitrous acid.[20] Rapid preequilibration between 2 equiv of nitrous acid generates 1 equiv of the anhydride. At high $[NO_2^-]$, *e.g.*, 1.6 M, the deamination becomes pseudo first order in amine.

We demonstrated the micellar catalysis of deamination by alkylammonium ions.[9] To probe the catalysis more carefully, we studied the rate of deamination of 2-aminooctane as a function of C_i, and recorded the pseudo-k_1 values (see Table IV). Acidification was done with either HCl or $HClO_4$. The *initial extent of micellization*, F_m, was calculated from

$$F_m = (C_i - \text{cmc})/C_i$$

in which C_i is the initial amine concentration, and the cmc is taken from Table III. The reactions were followed manometrically by the procedures discussed in the Experimental Section and in ref 9.

Table IV. Rate Constants for Deamination of 2-Aminooctane as a Function of F_m[a]

Case	C_i, M	F_m	k_1, min^{-1}
1 ($HClO_4$)[b]	0.03[c]	0.00	0.037
2	0.11	0.47	0.26
3	0.13	0.54	0.35
4	0.22	0.74	0.41
5	0.24	0.76	0.46
6	0.44	0.87	0.50
1 (HCl)[d]	0.06[e]	0.00	0.05
2	0.135	0.33	0.25
3	0.17	0.47	0.36
4	0.20	0.55	0.37
5	0.25	0.64	0.45
6	0.40	0.77	0.56

[a] At 25°, 1.6 M $NaNO_2$, pH 4. [b] $HClO_4$ was used to adjust the acidity for these runs. [c] $C_i <$ cmc (0.058 M). [d] HCl was used to adjust the acidity for these runs. [e] $C_i <$ cmc (0.09 M).

The observed k_1 values increased with increasing micellization, a result characteristic of micelle-catalyzed processes.[11] *Below* the systemic cmc's (case 1), "normal" rate constants were observed. The value in the HCl case was, perhaps, a bit high, suggestive of a contribution of NOCl to the nitrosation (*i.e.*, catalysis by chloride).[4e] However, such contributions were unimportant in the micellar cases. Thus, inclusion of NaCl (0.11 M) in case 2 ($HClO_4$), Table IV, *lowered* k_1 from 0.26 to 0.24 min^{-1}. Increasing [NaCl] to 0.22 M furthered lowered k_1 to 0.22 min^{-1}.

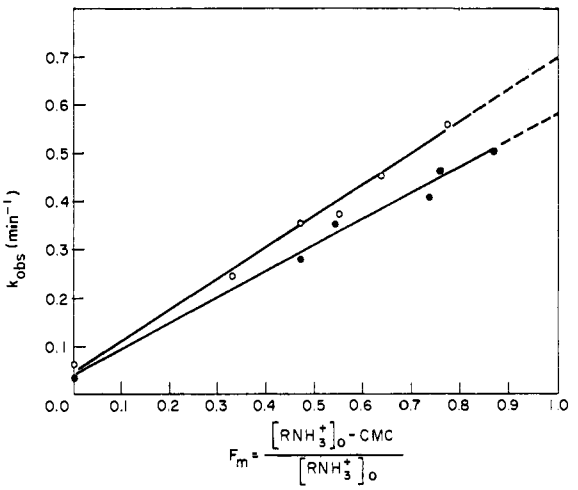


Figure 3. Pseudo-first-order rate constants, k_{obsd}, for the deamination of 2-aminooctane with 1.6 M $NaNO_2$, 25°, pH 4, *vs.* F_m. Open circles correspond to runs in which $HClO_4$ was the acidifying agent; solid circles correspond to runs which employed HCl acidification.

The deaminations at $C_i >$ cmc can be treated as sums of micellar (m) and nonmicellar (f) processes. The rate may be written

$$\text{rate} = k_1^{obsd}[RNH_3^+]_{total} = k_m[RNH_3^+]_m + k_f[RNH_3^+]_f \quad (1)$$

In eq 1, k_m and k_f are the pseudo-first-order rate constants for micellar and nonmicellar deaminations. This partition appears reasonable, because there will always be some free alkylammonium ions present (stoichiometrically ~ cmc), and because the association and dissociation of individual ammonium ions from the micelle should be much more rapid than the micelle-catalyzed deamination.[21]

Dividing (1) by $[RNH_3^+]_{total}$, we obtain (2), in which

$$k_1^{obsd} = k_m[RNH_3^+]_m/[RNH_3^+]_{total} + k_f[RNH_3^+]_f/[RNH_3^+]_{total} \quad (2)$$

$[RNH_3^+]_m/[RNH_3^+]_{total}$ is simply F_m, the extent of micellization, which, at least initially, may be defined in terms of C_i and cmc. $[RNH_3^+]_f$ can be equated with the cmc. Equation 2 can then be rewritten as

$$k_1^{obsd} = k_m F_m + k_f(1 - F_m) \quad (3)$$

At high values of F_m ($C_i \gg$ cmc), there is little contribution from the k_f term, and k_m can be extrapolated to 0.56–0.60 min^{-1} ($HClO_4$ deaminations) and ~0.7 min^{-1} (HCl deaminations). These extrapolations appear in Figure 3, in which k_1^{obsd} is plotted against F_m.

Interestingly, (2) or (3) can also be written in the form (4). Taking, for example, k_f = 0.037 min^{-1} (Table IV,

$$k_1^{obsd} = k_m(C_i - \text{cmc})/C_i + k_f(\text{cmc}/C_i) \quad (4)$$

(20) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, p 294.

(21) P. J. Sams, E. Wyn-Jones, and J. Rassing, *Chem. Phys. Lett.*, 13, 233 (1972), and references therein. See also N. Muller, *J. Phys. Chem.*, 76, 3017 (1972).

case 1, $HClO_4$), and k_1^{obsd} values of 0.35 and 0.50 min^{-1} (cases 3 and 6), we can solve simultaneous equations, based on (4), in which the unknowns are k_m and cmc. We find k_m = 0.56 min^{-1} and cmc = 0.050 *M*. Not surprisingly, the former value agrees with the graphical extrapolation. The latter value represents a *kinetic determination of the effective, systemic cmc*, which is in reasonable agreement with the value measured in model systems (0.058 *M*, see above).

The stoichiometric, third-order rate constant, k_3, is measured in terms of nitrite and alkylammonium ions (eq 5). Though these are the major ionic species

$$\text{rate} = k_3[RNH_3^+][NO_2^-]^2 \quad (5)$$

present, the rate-determining step involves the reaction of free amine with nitrous anhydride, for which (6)

$$\text{rate} = k_{real}[N_2O_3][RNH_2] \quad (6)$$

can be written. From (6), we can derive (7) by in-

$$\text{rate} = k_{real}K_{eq}^{N_2O_3}[NO_2^-]^2[H^+]K_A^{RNH_3^+}[RNH_3^+]/(K_A^{HNO_2})^2 \quad (7)$$

sertion of the proper equilibrium constants and concentration terms. Here, $K_{eq}^{N_2O_3}$ represents the equilibrium constant for the formation of N_2O_3 from HNO_2, and the acidity constants have their normal meanings. Eliminating the left-hand side of (5) and (7), and dividing by $[RNH_3^+][NO_2^-]^2$, we obtain (8). The

$$k_3 = k_{real}K_{eq}^{N_2O_3}K_A^{RNH_3^+}[H^+]/(K_A^{HNO_2})^2 \quad (8)$$

linearity of k_3^{obsd} and hydrogen ion concentration, demanded by (8), was separately demonstrated.[22]

The observed rate constant depends, therefore, on several equilibrium constants which represent rapid processes occurring prior to the rate-determining nitrosation. Micellar effects on the latter are likely to be small, and we inquire how transfer of the deaminative system from the bulk aqueous phase to the (cationic) micellar phase affects the preequilibria.

Electrostatic interactions between the positive ammonium ion head groups of the micelles will destabilize *protonated* amine relative to the free base, and $K_A^{RNH_3^+}$ will be augmented upon micellization of the alkylammonium ions; this will enhance k_3. Cordes has reported a 15-fold enhancement of K_A attending the solubilization of an iminium ion in cetyltrimethylammonium bromide micelles.[23] This is just the proper magnitude of K_A increase to account for our results. We suggest, therefore, that the micellar catalysis of deamination occurs because, at an externally imposed, constant pH, the available *free* (nitrosatable) amine is increased by micellization, which is reflected in a larger k_3^{obsd}.[24,24a]

(22) From pH 3.4 to 4.75, the deamination of 2-aminobutane, under standard conditions, followed $k_1^{obsd} = 0.041(10^4[H^+]) + 0.44 \times 10^{-4}$. The correlation coefficient indicated significance with greater than 99.9% confidence.[2b]

(23) M. T. A. Behme and E. H. Cordes, *J. Amer. Chem. Soc.*, 87, 260 (1965), and references therein.

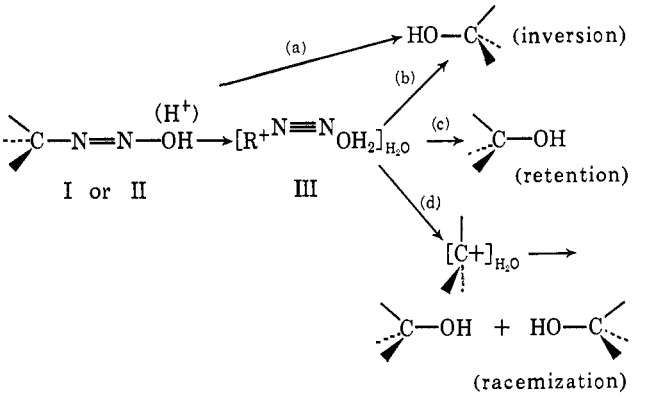
(24) "In terms of a thermodynamic cycle relating free and micellized amine and ammonium ion, the micelle "selects" amine from the bulk phase in preference to ammonium ion, for there is no unfavorable electrostatic interaction attending the solubilization of amine, whereas work must be done against the micellar field in order to solubilize the ammonium ion."[1]

(24a) NOTE ADDED IN PROOF. Micellar catalysis has recently been observed in the deamination of *O*-alkyl hydroxylamines: M. Hutchinson and G. Stedman, J. *Chem. Soc., Perkin. Trans. 2*, 93 (1973). We believe that this catalysis can be interpreted similarly to our own cases.

Stereochemistry. The stereochemistry of the deaminative amine → alcohol transformation depends strongly on the structure of the amine, and much discussion has been lavished on the mechanistic details.[4a-d,g] We will require a moderately close look at this material for our own discussion.

The alkane diazotic acid (I) arises by tautomerism of the *N*-nitrosoamine which is formed in the rate-determining step (see above). Intermediate I can be converted to alkanol by one or more of several competing pathways, each of which possesses a characteristic stereochemistry. The weighted sum of the competing pathways then generates the stereochemical outcome of a given deamination. The argument is illustrated by Scheme I.

Scheme I



The product alcohol could come from (a) inverting attack of water on I or II (protonated diazotic acid); (b) inverting hydrolysis of III, an alkyl cation, separated from its original OH or OH_2 unit by the ejected nitrogen molecule; (c) frontside return, within III, of either the original OH unit, or of a water molecule hydrogen-bonded to it (stereochemical retention); or (d) racemizing capture, by water, of a symmetrically hydrated alkyl cation derived from III. Scheme I omits explicit reference to an alkyldiazonium ion, but such intermediates are important when the alkyl group is primary.[4d] In that instance the expected deaminative sequence should be: (I or II) → RN_2^+ → HOR (inversion), which avoids the intermediacy of a primary alkyl cation.[4c]

Scheme I is not appropriate for a normal solvolytic process, *e.g.*, the hydrolysis of 2-octyl mesylate, in which the overall activation energy may be ~30 kcal/mol, and the differential activation energies between the pathways could be ≥2 kcal/mol. The loss of nitrogen from species such as I or II, however, may require an activation energy as low as 3–4 kcal/mol,[4g] in which case, the differential activation energies should be quite low (~1 kcal/mol). Effective competition between the pathways would then be possible in the deaminative process, whereas it would not be anticipated in the solvolysis.[25a]

Thus, 1-aminobutane-*1-d* was converted by nitrous and acetic acids to butyl acetate with ~69% net inversion,[25b] consistent with much SN2-like attack of acetic acid on either butane 1-diazotic acid or on the

(25) (a) In fact, the hydrolysis of 2-octyl mesylate occurs with 99% inversion. For a review, see D. J. Raber and J. M. Harris, *J. Chem. Educ.*, **49**, 60 (1972). (b) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, 79, 288 (1957).

n-butyldiazonium ion. Path (a) was dominant, and the 1-butyl cation was largely avoided. With 2-aminobutane, increasing contributions from paths (c) and (d) are expected, for the potential cation (*sec*-butyl) is energetically less objectionable. Indeed, the conversion of this amine to 2-butanol proceeded with only 22–23% net inversion.[6,26]

A series of optically active 2-aminoalkanes (C_4–C_{10}) was deaminated under standard conditions, at C_i = 0.76 *M*.[8] We observed that the stereochemistry of 2-alkanol formation changed from the normal ~22% net inversion (2-aminobutane, 2-aminopentane, 2-aminohexane), through near-racemization (2-aminoheptane), to net retention (2-aminooctane, 2-aminodecane). The shift of the stereochemistry toward retention coincided with the *onset of alkylammonium ion micellization* (*i.e.*, it began when C_i > cmc).

We next began a thorough study of the deaminative stereochemistry of 2-aminooctane; our working hypothesis was that a micellar environment could bias the competition of pathways (see Scheme I) in favor of (c), and thus lead to enhanced retention. It was already known that homogeneous deamination reactions gave increasing retention as the environment was altered from water to less polar solvents.[4c]

We have described the resolution of 2-aminooctane,[6,27] a standard method for its deamination,[6] the isolation of product 2-octanol,[6] and the determination of the latter's optical purity by either polarimetry or by gc analysis of derived L-acetyllactate diastereomers.[5a] Additional products of the deamination reactions have also been described.[6,8] In Table V are the stereochemical results of a series of 2-aminooctane deaminations (standard conditions), as a function of C_i.

Table V. Stereochemistry of the 2-Aminooctane → 2-Octanol Transformation; Observations and Calculations[a]

C_i, *M*[b]	F_m[c]	Stereochemistry of 2-octanol (% net) Obsd	Calcd[d]
0.76	0.92	6 (retn)	
0.39	0.85	Racemization	1.5 (retn)
0.15	0.61	7 (inv)	5.7 (inv)
0.083	0.30	16.3 (inv)	15 (inv)
0.076	0.24	18 (inv)	17 (inv)
0.029	0.00[e]	25 (inv)	
0.015	0.00[e]	23 (inv)	

[a] At 25°, pH 4, 1.6 *M* $NaNO_2$, acidified with $HClO_4$. The 2-octanol stereochemistry was determined by gc,[5a] and each entry is the mean of at least two experiments. Reproducibility was ~±1.5 stereochemical units. [b] Initial [2-Oct-NH_3^+]. [c] Calculated from $(C_i - \text{cmc})/C_i$, with cmc = 0.058 *M* (see Tables II and III). [d] See text. [e] Below the cmc.

Below the systemic cmc, 2-octanol is formed with the inversion stereochemistry normally expected in the deamination of a *sec*-carbinamine. Above the cmc, however, the stereochemistry moves toward racemization, crossing over at $F_m \sim 0.85$, and reaching 6% net *retention* at $F_m \sim 0.92$. This behavior parallels the kinetic phenomena described above; it can be treated as the composite outcome of a nonmicellar deamination which occurs with normal stereochemistry, and a micellar deamination which occurs with retention.

A semiquantitative model of the stereochemical dependence on micellization can be constructed if the reaction is considered to occur in two stages. First there is a micellar deamination which affords 2-octanol with ~6% net retention. After [2-Oct-NH_3^+] has been so reduced that $F_m = 0$, a nonmicellar deamination converts the residual 2-octylammonium ion to 2-octanol with ~24% net inversion. The assumption of discrete stages is not a bad one, because micellar deamination is *faster* than its nonmicellar counterpart (see above).

According to the model, we can write eq 9, which

$$\text{resultant stereochemistry} = S_m F_m + S_f(1 - F_m) \quad (9)$$

parallels the kinetic expression (eq 3). Here, S_m and S_f are the characteristic stereochemistries which we have observed for the micellar and nonmicellar deaminations, 6% net retention and 24% net inversion, respectively. F_m is the initial extent of micellization, defined above. Application of (9) gives the "calculated" stereochemical results shown in Table V; agreement between calculated and observed values is good.

It will be noted, however, that the observed values all lie to the inversion side of the calculated values. This probably reflects the small contribution of nonmicellar deamination which occurs *simultaneously* with the micellar deamination, and which affords 2-octanol with 24% net inversion. The two-stage model neglects this contribution, but the small size of the discrepancy indicates that the approximation is valid. The two-stage model also assumes that the efficiency of conversion of 2-aminooctane to 2-octanol is similar in both micellar and nonmicellar processes.

The results prove that a micellar environment can indeed alter the stereochemistry of a deamination reaction, and they are generally in keeping with the concept of a micellar environment which, being less polar than water,[11a] favors stereochemical retention. To underline these effects, *l*-2-aminooctane at 0.089 *M* was deaminated as a mixture with 0.77 *M* *dl*-2-aminodecane, under otherwise standard conditions. Table V suggests that, in the absence of the 2-aminodecane, 2-octanol would have been formed with ~16% net inversion. In fact, the alcohol was obtained with 5.4% *net retention*. In a second trial, 2-aminooctane (0.083 *M*) and 2-aminodecane (0.70 *M*) gave 2-octanol with 4.2% net retention.

We suggest that the 2-decylammonium ions comicellized with the 2-octylammonium ions, and that the latter, though present in rather low concentration, were caused to deaminate with stereochemistry characteristic of $F_m > 0.9$ (Table V, first entry).

An analogous experiment, in which a mixture of *l*-2-aminooctane (0.089 *M*) and *dl*-2-aminobutane (0.89 *M*) was deaminated, gave 2-octanol with 9.3% net inversion. In a second trial, with [2-Oct-NH_2] at 0.073 *M*, the alcohol was obtained with 10.2% net inversion. In contrast to 2-decylammonium ions, the short-chain 2-butylammonium ions do not self-micellize at concentrations below ~2 *M*.[8] They cannot, therefore, provide a micellar template to control the stereochemistry of deamination. But, in the presence of a high concentration of 2-butylammonium ions, the cmc

(26) K. B. Wiberg, Ph.D. Thesis, Columbia University, New York, N. Y., 1950.
(27) F. G. Mann and J. W. G. Porter, *J. Chem. Soc.*, 456 (1944).

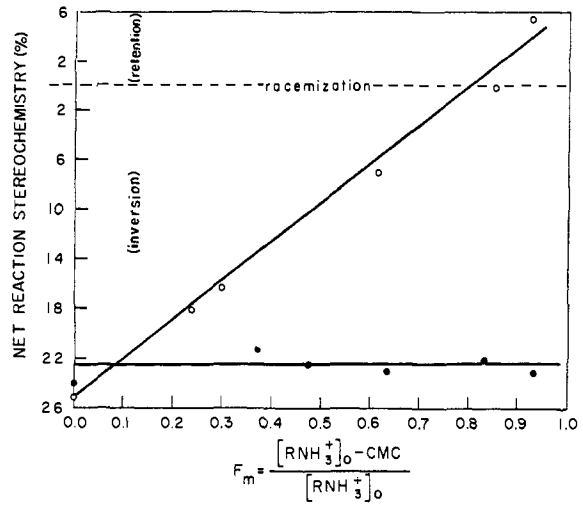


Figure 4. The stereochemical course of the 2-aminooctane → 2-octanol transformation with 1.6 *M* $NaNO_2$, 25°, pH 4, *vs.* F_m. Open circles correspond to runs in which $HClO_4$ was the acidifying agent; solid circles correspond to runs which employed HCl acidification.

of the 2-octylammonium ions will be lowered.[12] Indeed, the cmc of 2-octylammonium ion in the presence of 2-butylammonium ion was determined in a model system, and found to be 0.048 *M*, substantially lower than the 0.058 *M* found previously (Table II). Equation 9 predicts that the deamination of 2-aminooctane with C_i = 0.089 *M* and cmc = 0.048 *M* should give 2-octanol with ~10% net inversion, in good agreement with the observed result.

In view of the counterion effects yet to be discussed, it is worth pointing out that the micellar stereochemical effect is "saturated" when at least 1 equiv of perchlorate is initially present for each equivalent of 2-octylammonium ion. Thus, deamination of 2-aminooctane at 0.095 *M*, acidified with $HClO_4$ (to pH 4), in the presence of 0.078 *M* added $NaClO_4$, gave 2-octanol with 17.2% net inversion. 2-Aminooctane at 0.2 *M*, with 0.2 *M* added $NaClO_4$, afforded 2-octanol with 3.6% net inversion. Both results are similar to those obtained in the *absence* of excess perchlorate (see Table V).

Counterion Effects. We first studied the deamination of *l*-2-aminooctane with $NaNO_2$–HCl, carrying out a series of experiments at differential initial amine concentrations. Excepting the change in mineral acid, the reaction conditions were identical with those described above. Little 2-chlorooctane (<2.5%) was formed in these reactions. The results are collected in Table VI, in which F_m is calculated from C_i and cmc, taking the cmc as 0.09 *M* (see Tables II and III).

Table VI demonstrates that the *micellar control of stereochemistry has disappeared in the absence of perchlorate anions.* But these deaminations (F_m > 0) were definitely micellar, for they were accelerated (see Table IV and Figure 3). Comparison of Table VI with Table V highlights the counterion effect.

The striking contrast between perchlorate and chloride micellar deaminations is further shown in Figure 4, which graphically presents the data of Tables V and VI. Figure 4 should be compared with Figure 3, in which the micellar kinetic effects are similarly presented as a function of counterion. Although k_1 showed strong dependence on F_m irrespective of counterion, the stereochemical results show a lack of dependence on F_m when the counterion is chloride.

Table VI. Stereochemistry of the 2-Aminooctane → 2-Octanol Transformation, Chloride Counterions[a]

C_i, *M*[b]	F_m[c]	Stereochemistry, % net inv
1.29	0.93	24
0.53	0.83	23
0.245	0.635	22.9
0.17	0.47	22
0.14	0.37	21
0.015–0.067[d]	0.0	23.9 ± 1.0

[a] At 25°, pH 4, 1.6 *M* $NaNO_2$, acidified with HCl. The 2-octanol stereochemistry was determined by gc,[8a] and the reproducibility was generally within 1 stereochemical unit. [b] Initial [2-Oct-NH_3^+]. [c] From $(C_i - cmc)/C_i$. [d] Four experiments (C_i < cmc) were carried out over this concentration range.

The evidence now suggests a *cooperative micelle–counterion* control of stereochemistry. The anion dependence was highlighted by additional experiments.

(a) Deamination of 0.067 *M* *l*-2-aminooctane, mixed with 0.46 *M* *d,l*-2-aminodecane, with $NaNO_2$–HCl gave *d*-2-octanol with 21.4 ± 0.5% net inversion. In contrast to the analogous $NaNO_2$–$HClO_4$ experiment (see above), *no* stereochemical control was provided by the 2-decylammonium micelles in the presence of chloride counterions.

(b) Deamination of *l*-2-aminooctane (0.394 *M*) with $NaNO_2$–HCl and 0.197 *M added* $NaClO_4$ gave *d*-2-octanol with 7.0% net inversion. A measure of stereochemical control was thus restored by the addition of ~0.5 equiv of perchlorate.

(c) Bromide, like chloride, was not effective in cooperative micellar stereochemical control (see also below). Thus, deamination of 0.067 *M* *l*-2-aminooctane with $NaNO_2$–HCl in the presence of 0.47 *M* (micellar) *d,l*-2-OTA-Br gave *d*-2-octanol with 27.3% net inversion. An analogous experiment could not be carried out in the presence of perchlorate, however, because 2-OTA-ClO_4 was not sufficiently soluble in water.

The perchlorate–chloride contrast led us to study other counterions. First we determined the cmc of 2-octylammonium ions in the presence of each of the new counterions (see above and Table III), so that F_m could be estimated for each subsequent deamination. *l*-2-Aminoooctane was then deaminated in 1.6 *M* $NaNO_2$; the pH was adjusted to 4.0 with HX. For each counterion, micellar and nonmicellar (C_i < cmc) deaminations were carried out; both pseudo-first-order rate constants and stereochemical results were recorded. Table VII collects the data.

We note that bromide and acetate join chloride (and, by implication, nitrite) as anions which cannot provoke micellar stereochemical control. However, the kinetic results prove that micellar deaminations were effectively catalyzed in the presence of these anions. Camphorsulfonate, fluoroborate, and *p*-tosylate (increasingly in that order) join perchlorate as cooperative counterions, which assist in the display of micellar stereochemical control.

The anions which are effective in stereochemical control are relatively *hydrophobic*, and are expected

Table VII. Micellar Deamination of 2-Aminooctane. Anion Dependence of Kinetics and Stereochemistry[a]

Anion	$[RNH_2]_i$, M	F_m[b]	Stereochemistry (% net inv) Obsd	Normal[c]	k_{obsd}, min^{-1} Obsd	Normal[c]
Br^-	0.340	0.79	22.2	23.4	0.420	0.031
CH_3COO^-	0.300	0.70	23.4	23.9	0.400	0.035
d-$C_{10}H_{15}SO_4^-$[d]	0.380	0.89	17.3	25.4	0.252	0.044
BF_4^-	0.410	0.82	14.7	23.1	0.200[e]	0.036
p-$C_7H_7SO_3^-$[f]	0.360	0.92	7.3	23.3	0.133[g]	0.030

[a] Standard deamination conditions were used; pH 4 was adjusted with HA. [b] Calculated from $(C_i - cmc)/C_i$, using the indicated initial amine concentration and the appropriate cmc value from Table III. [c] $C_i <$ cmc. [d] d-10-Camphorsulfonate. [e] At $C_i = 0.422$ M, $F_m = 0.82$. [f] p-Toluenesulfonate. This reaction was done at 29°. [g] At $C_i = 0.306$ M, $F_m = 0.90$.

Table VIII. Properties of Anions and the Stereochemical Control of Micellar Deamination Reactions

Anion	Control[a]	$\Delta H°_{298}$ (hydration)[b]	Aff. Dowex 2[c]	N[d]
ClO_4^-	+	−57.1	32	11.8
p-$C_7H_7SO_3^-$	+		14	
BF_4^-	+	−71.2		
Br^-	-	−79.8	3.4	11.3
NO_2^-	e			10.1
Cl^-	-	−87.6	1.0	10.0
CH_3COO^-	-		0.17	
F^-	f	−121.9	0.10	4.8

[a] Ability to influence the stereochemistry of the micellar deamination of 2-aminooctane; see Table VII. [b] In kcal/mol, see ref 29. [c] H. P. Gregor, J. Belle, and R. A. Marcus, *J. Amer. Chem. Soc.*, 77, 2713 (1955). [d] The lyotropic number; the relative ability of NaX to salt agar out of water. N_{Cl^-} and $N_{SO_4^{2-}}$ are defined as 10.0 and 2.0, respectively (see ref 16). [e] Normally present during deamination. Because Br^- does not assist micellar stereochemical control, NO_2^-, which has a lower N value, probably does not. [f] Not studied.

to bind strongly to alkylammonium ion micelles.[28] The data compiled in Table VIII support the contention that perchlorate, fluoroborate, camphorsulfonate, and p-tosylate are, indeed, hydrophobic relative to chloride, bromide, nitrite, and acetate. The former ions are characterized by lower hydration enthalpies,[29] higher affinities for Dowex 2 (a tetraalkylammonium ion resin), and higher lyotropic numbers. Light-scattering studies independently demonstrate that these anions are strongly bound to cationic micelles and highly effective in charge neutralization of the micellar head groups.[18,28] Similar conclusions stem from studies of the comparative counterion inhibition of the cationic micellar catalysis of the basic hydrolysis of esters.[11]

With the new information, a microscopic mechanism for micellar stereochemical control can be constructed by elaboration of Scheme I. We maintained that the stereochemical outcome of a deamination reaction was the sum of competitive processes: inverting solvolysis, frontside return (or its equivalent) with retention, and racemizing capture of a hydrated carbonium ion. Now we suggest that this analysis holds for deamination in the highly aqueous Stern layers of alkylammonium ion micelles which are *weakly* associated with their counterions (Cl^-, Br^-, CH_3COO^-, NO_2^-), and that the resultant of the stereochemical partition in such micelles is precisely that which obtains in the *absence* of micelles: >20% net inversion.

On the other hand, the poorly hydrated[29] counterions (ClO_4^-, BF_4^-, $CamSO_3^-$, p-Tos^-) are strongly bound.[28] They afford larger, more effectively charge-neutralized, denser, and less aqueous micelles.[18,28,30a] In such micelles, return processes should make a larger contribution to the amine → alcohol conversion. Accordingly, the stereochemistry should move toward retention.[30b]

The mechanism outlined here has the virtue of bridging homogeneous and micellar deamination reactions. The stereochemistry of the former moves toward retention as the solvents are varied from water to less polar media, and explanations have been offered in terms similar to those of Scheme I.[4a,4c] In a sense, then, the micellar stereochemical control is a species of solvent effect in which the polarity varies as a function of the counterion.

The increased retention observed in micelle–perchlorate deaminations might alternatively be attributable to a "double-inversion" process, in which tightly bound perchlorate ions first displace nitrogen, with inversion, from the product-forming intermediates (Scheme I: I, II, or III). The unstable, inverted alkyl perchlorate thus formed would be subject to rapid, inverting hydrolysis. The double inversion would generate 2-octanol with net retention. We cannot yet eliminate this alternative, but we prefer the "altered micelle" concept for the following reasons.

(a) Addition of *excess* perchlorate to micellar $NaNO_2$–$HClO_4$ deaminations *did not significantly enhance* the observed stereochemical control (see above). One might expect a double-inversion mechanism to operate over a wide range of perchlorate concentrations, and retention to increase steadily with added perchlorate. The absence of this response appears to favor the altered micelle mechanism, but it is conceivable that the micelles are "saturated" with perchlorate at $[RNH_3^+]/[ClO_4^-] \sim 1$, and that stereochemical control is maximized at this point.[31]

(b) More cogent evidence for the altered micelle idea is afforded by preliminary studies of micellar deaminations in which 2-aminooctane (C_i = 0.68–0.75 M) was deaminated with 1.5 M $NaNO_2$ and 1 equiv of a *mixture* of hydrochloric and perchloric acids.[32]

(28) R. D. Geer, E. H. Eylar, and E. W. Anacker, *J. Phys. Chem.*, 75, 369 (1971); E. W. Anacker and R. D. Geer, *J. Colloid Interface Sci.*, 35, 441 (1971). See also ref 18, and R. P. Taylor and I. D. Kuntz, Jr., *J. Amer. Chem. Soc.*, 94, 7963 (1972).

(29) The thermodynamics of anion hydration are discussed by H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, 59, 1126 (1963); *J. Chem. Soc.*, 4603 (1960). See, also, S. Subramanian and H. F. Fisher, *J. Phys. Chem.*, 76, 84 (1972).

(30) (a) Additional examples of the structural alteration of micelles by salts have recently been reported by M. Shinitzky, A.-C. Dianoux, C. Gitler, and G. Weber, *Biochemistry*, 10, 2106 (1971). (b) Attempts to study micellar deaminations in the presence of hydrophobic anions such as tetraphenylborate, trichloroacetate, or picrate were defeated by precipitation of the alkylammonium salts.

(31) Even at $[RNH_3^+]/[ClO_4^-] = 1$, however, perchlorate must still compete for micellar sites with the large excess of nitrite which is present. *Some* response to additional perchlorate would be anticipated.

(32) Because a high C_i was chosen, F_m varied only from 0.87 to 0.91 over the entire composition range of the mineral acid mixture. (F_m was calculated from C_i and cmc, with the latter taken as 0.09 M for 100% HCl and as 0.058 M for 100% $HClO_4$.) The minimal variation of F_m ensures that the stereochemical results of these experiments do not simply reflect an alteration in F_m as a function of the changing chloride–perchlorate blend.

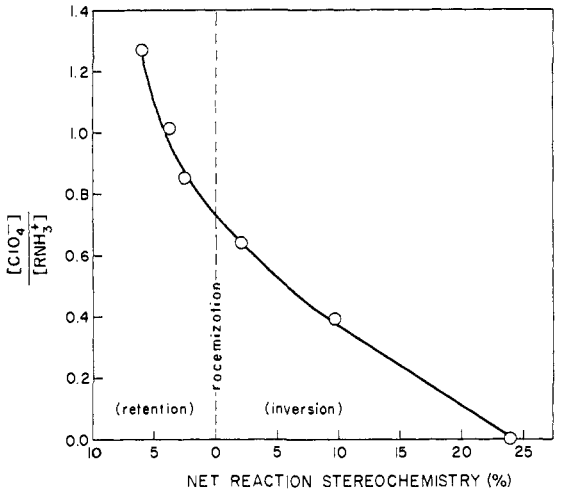


Figure 5. The stereochemical course of the 2-aminooctane → 2-octanol transformation $[RNH_3^+] \sim 0.7\ M$, $F_m \sim 0.9$, with 1.5 M $NaNO_2$, 25°, pH 4 (abscissa) *vs.* $[ClO_4^-]/[2\text{-octylammonium ion}]$ (ordinate). A blend of HCl and $HClO_4$ was the acidifying agent (see Table IX and text).

Table IX. Micellar Deamination of 2-Aminooctane. Stereochemical Dependence on Counterion Blend[a]

$[HClO_4]/[HClO_4 + HCl]$[b]	$[ClO_4^-]/[RNH_3^+]$[c]	Stereochemistry of $RNH_2 \rightarrow ROH$ (% net)[d]
0.00	0.00	~24 inv[e]
0.30	0.39	9.6 inv
0.50	0.64	2.0 inv
0.67	0.85	2.4 retn
0.80	1.01	3.7 retn
1.00	1.27	6 retn[f]

[a] Corco Reagent Grade (37–38%) HCl and MCB Reagent Grade (70–71%) $HClO_4$ were blended. [b] Composition of acidifying reagent. [c] The sum of added HCl and $HClO_4$ exceeds the initial concentration of 2-octylammonium ion, because some acid is used to protonate nitrite ion (see above), and the total $[X^-]$ introduced with the acidifying reagent is equal to $[RNH_3^+] + 0.19\ M$. The ammonium ion concentration was ~0.7 M for all runs of Table IX; the extra 0.19 M anion comes from the acid used to protonate the nitrite ions at pH 4 (see above[19]). The perchlorate concentration can therefore be approximated by $0.89y$, where y is the mole fraction of $HClO_4$ in the $HClO_4$–HCl acidifying blend. [d] Determined by the gc method. The % standard deviation was below 0.7%. [e] See Table VI, first two entries. [f] See Table V, first entry.

The results are gathered in Table IX, and displayed graphically in Figure 5. It appears that the cooperative micelle–anion stereochemical control is not a linear function of $[ClO_4^-]/[RNH_3^+]$ in the region below $[ClO_4^-]/[RNH_3^+] \sim 1.0$. Above ~0.65, additional perchlorate affords little additional control. This behavior seems more in keeping with an altered micelle mechanism than with a double-inversion process. A more linear stereochemical response to $[ClO_4^-]$, at least up to $[ClO_4^-]/[RNH_3^+] \sim 1$, would be expected of the latter mechanism, for it is essentially a "probability" mechanism. That is, the higher the perchlorate concentration *at* the micelle, the greater the chance that a decomposing diazotic acid will be properly aligned with an adjacent perchlorate ion, and the greater the chance for double inversion.

The stereochemical micellar salt effects differ from the more commonly observed competitive inhibitions of micelle-catalyzed reactions, which involve exclusion of an ionic reactant from an oppositely charged micelle (in which the substrate resides) by a more strongly bound but chemically impotent ion. In the present example, we believe, the micelles themselves have been altered through strong binding of certain counterions which, though not incorporated into product, modify product formation in the micelles of which they are a part.

Perhaps the closest parallel is to be found in Bunton's studies of the micellar catalysis of certain decarboxylation reactions.[33] Here, too, alteration of micellar structure by added salts was interpreted to "show how a reaction at a micellar surface can be controlled by chemically inert adducts...".[34]

Other examples of stereochemical micellar control are rare. Bunton's group has reported the stereoselective hydrolysis of chiral esters catalyzed by chiral micelles,[35] and the mutarotation of 2,3,4,6-tetramethyl-α-D-glucose can be enhanced by inverse micelles.[36] We believe that additional examples await discovery. We can, however, report a failure. The micellar deamination of *dl*-2-aminooctane, in the presence of the *d*-10-camphorsulfonate counterion, gave *rac*-2-octanol. Apparently, the diastereomeric cation–anion interactions were too weak to cause "asymmetric deamination."

Finally, we note that the counterion effects on the *kinetics* of micellar deamination (Table VII) show a potency order different from the one operative in stereochemical control. The kinetic order (decreasing catalysis) appears to be: $Cl^- \sim ClO_4^- > Br^- \sim CH_3COO^- > CamSO_3^- \sim BF_4^- > p\text{-}Tos^-$.

Excepting the location of ClO_4^-, the kinetic sequence appears in keeping with reduced catalysis as the anticipated binding of the counterion increases. This is sensible, for the kinetic effects depend on electrostatic interactions of the ammonium ion head groups. Greater counterion binding will result in greater charge neutralization, and will inhibit the catalysis (*i.e.*, reduce $K_A^{RNH_3^+}$). We do not understand why perchlorate micelles are so much better catalysts than (*e.g.*) fluoroborate micelles.

Experimental Section[37]

Reagents.[38] **2-Aminooctane** was purchased from K & K Laboratories, and was purified by distillation from sodium over a Vigreux column. Gc on a 12 ft × 0.35 in. 28% Penwalt, 5% KOH column, at 140°, demonstrated its purity. Purified amine was stored over Linde 4A Molecular Sieves in a desiccator (desiccants: KOH and $CaCl_2$).

2-Octyltrimethylammonium bromide (2-OTA-Br) was prepared from 2-aminooctane by the method of Moss and Sunshine,[13] and

(33) C. A. Bunton, A. Kamego, and M. J. Minch, *J. Org. Chem.*, 37, 1388 (1972).
(34) C. A. Bunton, M. Minch, and L. Sepulveda, *J. Phys. Chem.*, 75, 2707 (1971).
(35) C. A. Bunton, L. Robinson, and M. F. Stam, *Tetrahedron Lett.*, 121 (1971); *J. Amer. Chem. Soc.*, 92, 7393 (1970).
(36) E. J. Fendler, J. H. Fendler, R. T. Medary, and V. A. Woods, *Chem. Commun.*, 1497 (1971); *J. Amer. Chem. Soc.*, 94, 7288 (1972).
(37) The following instrumentation was employed: ir spectra, Perkin-Elmer Infracord; gc analyses, Varian Aerograph A90-P3 or 1720 (integration by cut-and-weigh of traces, thermal conductivity detectors); optical rotations, Rudolph polarimeter (neat liquids, 100 λ, 0.5-dm cell, mean of 10 readings, ±0.02°); melting points, Mel-Temp (uncorrected). Elemental analyses were done by Micro-Tech Laboratories, Skokie, Ill.
(38) All reagents were ACS Reagent Grade, and were used without further purification, unless otherwise specified.

had mp 257–258° dec (sealed tube). The literature value is 259–260° dec.[13] A further criterion of purity was the absence of minima in log (concentration) *vs.* surface tension experiments with aqueous solutions of the salt.[12c]

2-OTA-Cl was prepared in 68% yield from 2-OTA-Br by repetitive ion exchange on a column of Dowex 21K, type 1 resin.[39] The purified,[2b] dried (24 hr at 40° (0.8 Torr)), white crystals had mp 268–269° dec (sealed capillary), and gave a negative test for Br^- when shaken with chlorine water and CCl_4.

Anal. Calcd for $C_{11}H_{26}ClN$: C, 63.58; H, 12.61; Cl, 17.06; N, 6.74. Found: C, 63.64; H, 12.67; Cl, 17.26; N, 6.69.

2-OTA-NO_3 was prepared in 94% yield by repetitive ion exchange[39] of 2-OTA-Br.[2b] The deliquescent salt was dried at 55° (1 Torr), had mp 186–187° (sealed capillary), and gave a negative Br^- test with $AgNO_3$. The ir spectrum (KBr pellet) showed bands at 1360 and 845 cm^{-1}, compatible with nitrate ion.[40]

Anal. Calcd for $C_{11}H_{26}N_2O_3$: C, 56.38; H, 11.18; N, 11.95. Found: C, 56.17; H, 11.15; N, 11.77.

2-OTA-NO_2 was prepared in 76% yield from 2-OTA-Br. An acidified aqueous solution of the final product gave no precipitate with $AgNO_3$, indicating the absence of bromide. The dried salt (40° (1 Torr), 24 hr) had mp 223–225° dec (sealed capillary). The ir spectrum (KBr pellet) showed absorptions at 1350, 1270 (strong), and 830 (weak) cm^{-1}, consistent with ionic nitrite.[41]

Anal. Calcd for $C_{11}H_{26}N_2O_2$: C, 60.51; H, 12.00; N, 12.83. Found: C, 60.60; H, 11.96; N, 12.86.

The newly prepared 2-OTA-X salts showed no minima in log (concentration) *vs.* surface tension experiments.

Cmc Determinations. The cmc's were determined from graphs of observed surface tension (γ) *vs.* log (concentration) of the various surfactants in aqueous solutions. "Lecktrostill Steam Distilled Water" (resistivity $> 1.5 \times 10^6$ ohm cm, Electrified Water Co., Newark, N. J.) was employed in all determinations. γ was measured with a Fisher automatic surface "Tensiomat" on aqueous solutions contained in a jacketed cell, thermostated at 25 ± 0.02° with a Haake constant-temperature circulating pump. The general procedure is described in ref 13. γ readings were taken in triplicate at each surfactant concentration; the mean values were reproducible to ±0.3 dyn/cm.

A sample cmc determination appears in Figure 1. The cmc was taken as the intersect of the two straight lines. Each line was determined by least-squares analyses of the four or five points most distant from the intersection point. Two separate cmc determinations were made for each surfactant, under each condition of interest.

Further discussion appears above; the results are shown in Tables I–III and in Figure 2.

Kinetic Studies. A three-necked, 100-ml round-bottom, jacketed flask was fitted with pH electrodes, a pressure-equalized addition funnel, and a stirring bar. Aqueous sodium nitrite (66 ml, 1.59 *M*, 10%) (Baker reagent grade), and a known quantity of 2-aminooctane (0.7–3.5 g) were added to this vessel, and the mixture was acidified with HX (added from the addition funnel) to pH 4.0.[42] The rapid acidification initiated gas evolution, and was taken as time zero. The now-homogeneous reaction solution was stirred magnetically, and held at 25° by water circulated through the flask jacket with a Haake constant-temperature circulating pump. The evolved gases exited through the top of the addition funnel, and were conducted through a concentrated H_2SO_4 scrubber and a saturated aqueous Na_2CO_3 scrubber to a gas buret.[43]

The gas buret could be read to ±2 ml, and had a capacity of 500 ml. Readings of volume were taken every 10 sec, at atmospheric pressure (maintained by a leveling bulb which could be rapidly raised or lowered by a Big Jack). Nitrogen evolution was usually followed for ~15 min, corresponding to 50–90% of reaction.

The reaction was first order in amine and second order in nitrite. k_2 was determined from the integrated rate law. It deviated negatively after 20–35% of reaction, presumably because of nondeaminative destruction of nitrous acid.[44] The reaction was also pseudo first order in 2-aminooctane. The k_1 values of Table IV were determined from initial portions of the kinetic runs. For further discussions of the kinetic order, and the observed rate constants, see ref 2b and 9.[45]

Control experiments were carried out to exclude collection of nitrogen oxides as a complicating factor in these manometric studies. (a) A blank reaction (no amine) evolved only 4 ml of collected gas after 30 min. (b) With *no* scrubbers in the system, the deamination of nonmicellar *2-aminoheptane* gave $k_1 = 0.44$ min^{-1}, as compared with the normal value (with scrubbers) of $k_1 = 0.033$ min^{-1}. It is clear from these experiments that some scrubbable gases do contribute to the manometric rate constants, but that they can be removed. (c) A blank reaction, run for 5.5 hr, afforded a gas sample for ir analysis: 2250, 2226, 1280, and 1259 cm^{-1} (N_2O); 1910 and 1863 cm^{-1} (NO); 1785 and 1634 cm^{-1} (NO_2); and 2375 cm^{-1} (CO_2?).[46] (d) The ir of the evolved gases from a sub-cmc deamination of 2-aminobutane (>75% of reaction) showed no NO or NO_2 and only very weak N_2O absorptions. From intensity *vs.* partial pressure data for N_2O, its concentration in the collected (N_2) gas sample was estimated at <1%. (e) The evolved gases from a micellar deamination of 2-aminooctane (>80% of reaction) showed no nitrogen oxide ir absorptions. (f) Rate constants were unchanged upon prior purging of the reaction vessel with nitrogen.

We conclude that the manometrically determined initial rate constants are not significantly perturbed by nitrogen oxides generated under the reaction conditions.

Stereochemical Studies. 2-Aminooctane was resolved by the method of Mann and Porter.[27] *l*-2-Aminooctane was dried over BaO and distilled from sodium before use. Optical rotations[37] were compared with $\alpha^{19}D$ −2.66° (0.5 dm, neat)[47] in order to determine optical purity.

Deaminations of *l*-2-aminooctane were carried out as described under the kinetic studies. A related description of this reaction has been published in full detail, *including* the work-up and isolation procedures.[6] Reactions were run to >95% of completion (as judged by evolved nitrogen), and quenched by addition of aqueous Na_2CO_3 until pH 10. To determine its optical purity, the gc[48] isolated 2-octanol was studied either polarimetrically[37,49] or by quantitative conversion to the L-acetyllactate diastereomers.[5a]

The diastereomers were separated on a 24 ft × 0.25 in., 10% TCEP on 45–60 GCR column, operated at 160°, with a helium flow of 86 ml/min. The first diastereomer eluted contained the "1-octyl" residue.[50] Integration of the gc peak areas was done by cut-and-weigh of Xerox copies of the traces. Three Xerox copies of each trace and three traces of each gc sample were made and evaluated. Reproducibility to the mean value of the peak ratio was ±1.5%.

Miscellany. pH readings were shown to be independent of sodium ion concentration at pH 4.0, up to 1.59 *M* sodium chloride. The pH reading of dilute aqueous $HClO_4$ (at pH 3.55) was essentially unchanged when the solution was made 1.0 *M* in 2-OTA-Br (pH 3.59). Thus neither micelles nor sodium ions impaired our ability to monitor the pH of the various deamination reactions.

The *d*-10-camphorsulfonic acid[52] (Eastman Kodak) was re-

(39) General experimental techniques were taken from W. Rieman, III, and H. F. Walton, "Ion Exchange in Analytical Chemistry," Pergamon Press, New York, N. Y., 1970, p 63 ff. Specific details for each exchange synthesis appear in the Ph.D. Thesis of C. J. T.[2b] Dowex 21K resin was used in all syntheses.

(40) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 31.

(41) K. Nakanishi, "Infrared Absorption Spectroscopy-Practical," Holden-Day, San Francisco, Calif., 1962, p 57.

(42) The Leeds and Northrup pH meter, the Calomel, and measuring electrodes were standardized at pH 4.0 and 7.0 with M. C. B. buffer solutions.

(43) The H_2SO_4 scrubber removed gaseous olefinic products; the Na_2CO_3 scrubber removed nitrogen oxides.

(44) T. W. J. Taylor, *J. Chem. Soc.*, 1099 (1928).

(45) Examples of typical kinetic runs appear in the Ph.D. Thesis of C. J. T.[2b]

(46) Assignments are from: K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, pp 80, 101; G. M. Begun and W. H. Fletcher, *J. Chem. Phys.*, **28**, 414 (1958).

(47) F. G. Mann and J. Reid, *J. Chem. Soc.*, 3384 (1950). See also note (10) in ref 6.

(48) We used a 12 ft × 0.25 in., 18% Carbowax 20M on 45–60 GCR column. Operating conditions were: column, 148°; detector and injector, 250°; helium flow rate, 45 ml/min.

(49) $\alpha^{23}D$ +16.08° (2 dm, neat) is given for optically pure *d*-2-octanol by A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **78**, 5597 (1956).

(50) Since *l*-2-octanol and *l*-2-aminooctane are of the same optical series,[51] the stereochemical course of the reaction was readily determined.

(51) See M. Vogel and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 2262 (1966), and references therein.

(52) See Table VII.

crystallized twice from EtOAc. The dry acid decomposed at 193–194° (lit.[53] 195°), and had $\alpha^{24}D$ +0.490° (1 dm, *c* 0.0244, water). Based on $[\alpha]^{25}D$ 22.1°,[53] it was 92% optically pure.

(53) F. De Tar, *Anal. Chem.*, **41**, 1406 (1969).

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Mechanisms of Elimination Reactions. XX. Stereochemistry of Photoeliminations from Some Cyclic Phenylacetates[1]

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Abstract: Products and quantum yields were determined in the photolysis at 254 nm of cyclohexyl, *cis*- and *trans*-4-*tert*-butylcyclohexyl, *cis*- and *trans*-2-methylcyclohexyl, and *cis*- and *trans*-2-methylcyclooctyl phenylacetates. The major products are alkenes resulting from a type II photoelimination, though saturated hydrocarbons and other products derivable from free-radical processes can be found when the reaction mixtures are carefully examined. The photoelimination occurs more efficiently when the ester group is axial to the cyclohexane ring than when it is equatorial. In the 2-methylcyclohexyl system, the trans isomer yields about equal amounts of 1- and 3-methylcyclohexene, but the cis isomer yields mainly but not exclusively (*ca.* 90%) 3-methylcyclohexene. Both *cis*- and *trans*-2-methylcyclooctyl phenylacetates, however, yield a product mixture in which 3- predominates over 1-methylcyclooctene by about 3:1. These results indicate that the preferred, but by no means exclusive, mode of elimination is syn. The bearing of the results on the mechanism of photoelimination from esters is discussed.

The pyrolysis of esters to give olefins has been known for some time, and was comprehensively reviewed in 1960.[3] Its stereochemical course has been investigated by a number of groups who have shown it to be predominately or exclusively a syn elimination.[4–7] An analogous photoeliminaton has been found to occur,[8–10] but has been much less extensively investigated. The only published accounts of stereochemistry involve 1,2-dimethylbutyl esters. The phenylacetate eliminates at least 90% syn, once a sensitized isomerization of the first-formed product is allowed for,[11] while photoelimination from the acetate is less stereoselective.[12]

We undertook this research in order to gain greater insight into the mechanism and stereochemistry of ester photolysis. In this paper we will consider mainly the stereochemical aspects of the photoelimination. The effect of ring size and the nature of the excited states involved are discussed in an accompanying paper.[13]

We began with exploratory work on cyclohexyl benzoate, but abandoned that compound when reasonable photolysis times yielded no measurable amounts of cyclohexene. This observation is in line with a recent report that quantum yields are low in photoeliminations from benzoate esters[14] and with observations on 2-pentyl benzoate photolyses in our laboratories.[15] Cyclohexyl phenylacetate at 254 nm, however, gave modest quantum yields (0.03–0.05) when irradiated at 0.05–0.08 *M* in heptane, benzene, acetonitrile, tetrahydrofuran, *sec*-butyl alcohol, or *tert*-butyl alcohol. The quantum yields decreased somewhat with photolysis time, presumably due to quenching or competitive light absorption by products. The value for photolysis of 0.03 *M* cyclohexyl phenylacetate in hexane at 254 nm was 0.046 ± 0.002 when extrapolated to zero reaction. This and other relevant quantum yields are summarized in Table I.

We noted that the figure for cyclohexyl phenylacetate was distinctly lower than those found for open-chain phenylacetates (0.2–0.4)[15] or cyclopentyl phenylacetate (0.127 ± 0.015).[13] These differences made it evident that the efficiency of the photoelimination depended markedly on conformation. In order to explore this point further, we first chose the conformationally homogeneous systems *cis*- and *trans*-4-*tert*-butylcyclohexyl phenylacetate, which have the ester group axial and equatorial, respectively, to the ring. The results are given in Table I. The axial (cis isomer) ester group photoeliminates with a quantum yield approximately three times that of the equatorial (trans isomer) ester. The cis and trans esters also yield significant amounts of *tert*-butylcyclohexane.

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