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MICELLAR CATALYSIS OF THE NITROUS ACID DEAMINATION REACTION[1]

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Alkylammonium ion micelles alter the stereochemical course of the nitrous acid deamination reaction.[2] Although this reaction has been known since 1848,[3a] and the controversial nature of its kinetics much probed,[3b] we are yet able to report a new and fundamental catalysis of the nitrous acid deamination reaction.

Pure 2-aminoalkanes were deaminated with ca. 1.48 M aqueous sodium nitrite at 25 ± 0.2°; pH 4 was adjusted and maintained with 60% perchloric acid ("normal" conditions). The evolved nitrogen was scrubbed with concentrated sulfuric acid and with saturated aqueous sodium carbonate (or with potassium dichromate-sulfuric acid). Kinetics were followed manometrically; the collected gas showed neither nitric oxide nor nitrogen dioxide, and only traces of nitrous oxide (ir).[4]

The reaction was first order in amine and second order in nitrite (prior formation of N_2O_3 requires two nitrite ions).[3b,5-7] Third-order initial rate constants (k_3) were determined from the integrated rate law. (k_3 deviated negatively after 20-35% of reaction, presumably because of non-deaminating destruction of nitrous acid.[5]) The reaction was also pseudo-first-order in amine over this range (k_1). For example, deamination of 2-aminobutane at five initial concentrations (0.16-0.68 M) gave $k_1 = 0.044 \pm 0.003\ \mathrm{min}^{-1}$ and $k_3 = 2.2 \times 10^{-2}\ \mathrm{l}^2\ \mathrm{mol}^{-2}\ \mathrm{min}^{-1}$. The calculated k_1 (from k_3 and $[NO_2^-]^2$) was $0.048\ \mathrm{min}^{-1}$.[8] Nitrite dependence was checked at concentrations 0.33, 0.50, 0.75, 1.48, and 2.0 times "normal". As required, k_1 was altered by the square of these factors. Pseudo-first-order rate constants, obtained under the "normal" conditions, appear in Table I; satisfactory k_3 values were also obtained.

The rate constants are independent of concentration and (nearly) of chain

Table I. Kinetics of Nitrous Acid Deamination of $RCH(CH_3)NH_2$[a]

Case	R	[Amine], M.	k_1 ± av. dev.$_n$[b]	Cmc, M.[c]
1	C_2H_5	0.16-0.68	0.044 ± 0.003_5 min^{-1}	-
2	n-C_3H_7	0.23-0.68	0.030 ± 0.001_6	>1.81
3	n-C_4H_9	0.20-0.64	0.033 ± 0.002_3	0.89[d]
4	n-C_5H_{11}	0.20	0.034 ± 0.002_2	0.24[e]
5	n-C_5H_{11}	0.36	0.23 ± 0.01_3	0.24[e]
6	n-C_6H_{13}	0.22	0.41 ± 0.01_2	0.041-0.050[f]
7	n-C_6H_{13}	0.44	0.53 ± 0.03_2	0.041-0.050[f]

[a] Conditions as above. [b] Average deviation of n experiments. [c] Critical micelle concentration of $RCH(CH_3)\overset{+}{N}H_3$, determined by surface tensiometry, pH 4, 1.61 M $NaClO_4$.[2] [d] 0.83 and 0.87 M, respectively, in 1.61 M $NaNO_3$ and NaCl.[2] [e] 0.25 and 0.29 M, respectively, in 1.59 M $NaNO_3$ (pH 1) and NaCl (pH 3). [f] References (2) and (9).

Table II. Effects of Additives on the Deamination Reaction.[a]

Case	R in $RCH(CH_3)NH_2$	$[RNH_2]$, M.	Additive	(Conc. M.)	k_1 (min^{-1})
1	C_2H_5	0.18	NaBr	(0.29)	0.043
2	C_2H_5	0.18	OTA^+Br^-	(0.10)	0.046
3	C_2H_5	0.44	OTA^+Br^-	(0.27)	0.087
4	n-C_5H_{11}	0.18	NaBr	(0.29)	0.030
5	n-C_5H_{11}	0.18	$Et_4N^+Br^-$	(0.27)	0.043
6	n-C_5H_{11}	0.18	OTA^+Br^-	(0.11)[b]	0.075 ± 0.004_2
7	n-C_5H_{11}	0.18	OTA^+Br^-	(0.22)[b]	0.20
8	n-C_5H_{11}	0.18	OTA^+Br^-	(0.28)[b,c,d]	0.26

[a] Conditions as above. [b] HCl replaced $HClO_4$, with which heterogeneity was here observed. Both acids gave comparable results in cases 4 and 5, Table I. [c] k_1 = 0.26 min^{-1} with $HClO_4$. [d] Unaffected by added NaBr, 0.29 M.

length, as long as the initial alkylammonium ion[10] concentration is below the cmc; i.e., as long as micelles are absent (cases 1-4). Accelerations of 6-16 times are observed in the presence of alkylammonium ion micelles. Acceleration is greater, the more the initial ammonium ion concentration exceeds the cmc. The data suggest k_1(micellar) = 0.5-0.6 min^{-1}.

Table II demonstrates that the deamination of 2-aminoheptane can be catalyzed by micelles of 2-octyltrimethylammonium (OTA) ions.[9,11]

Neither sodium nor tetraethylammonium ions much affect the 2-aminoheptane deaminations (cases 4 and 5 *vs*. case 4, Table I). The long chain OTA ion, however, permits the formation of mixed micelles containing the 2-heptylammonium ion, and acceleration is observed (cases 6-8 *vs*. 4-5). The catalytic effect on a short chain amine is smaller; 2-butylammonium ion is less micellized by the OTA (cases 1-3).

Several factors can contribute to the observed micellar catalysis. The observed constants are related to the real rate constant (for reaction of N_2O_3 with amine)[3b] by factors which include dissociation constants for nitrous acid (inverse) and alkylammonium ion. Transfer of deamination from aqueous to micellar environments should alter these constants in such a way as to enhance $k_{observed}$.[12] (It seems less likely that k_{real} will be increased. A process in which two neutral species go to a polar transition state should not be enhanced by the decrease in medium polarity attending transfer from water to micelle.[13]) Additionally, the local concentration of nitrite ions should be increased in the region of the cationic micelles.[13]

The results have immediate application to synthetic and mechanistic deamination studies. Investigations of related phenomena continue in our laboratory.

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References

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(8) Rate constants are least-squares values, generally derived from 8-15 observations made over the initial 20% of each reaction. Fewer observations were made on the very rapid reactions.

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

(10) 2-Aminoalkanes are >99% protonated at pH 4.

(11) Cmc of OTA bromide is 0.15 *M* in 1.5 *M* aqueous NaBr. The cmc will be lowered in the presence of other alkylammonium ions; mixed micelles will form.

(12) With regard to micellar effects on alkylammonium ion dissociations, see the related work of M. T. A. Behme and E. H. Cordes, *J. Amer. Chem. Soc.*, **87**, 260 (1965).

(13) For a brief review of kinetics in micellar systems see: E. H. Cordes and R. B. Dunlap, *Accts. Chem. Res.*, **2**, 329 (1969).