Mechanisms of Buffer Catalysis in the Iodine Oxidation of *N*-Acetylmethionine

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Received September 4, 1981

The iodine oxidation of *N*-acetylmethionine is catalyzed by carboxylate anions. Linear catalysis is observed and a Brønsted coefficient of $\beta_{nuc} = 1.1$ is calculated. In the presence of buffers, the iodide dependence of the reaction rate is inverse squared. At very low buffer, however, the iodide dependence is more complex with apparent changes in order of inverse to inverse squared and inverse squared to inverse cubed as the pH is decreased. First-order rate constants, extrapolated to zero buffer concentration, suggest that the anion of *N*-acetylmethionine is the reactive form in the oxidation reaction. In the uncatalyzed reaction, *N*-acetylmethionine is 1400-fold more reactive than the corresponding methyl ester, suggesting intramolecular carboxylate catlaysis. However, the intramolecular reaction is only slightly more efficient than the intermolecular carboxylate catalyzed oxidation of the methyl ester, under the same conditions; an effective molarity of 2.3 M is calculated for these reactions. It is suggested that this low effective molarity results from a rate-limiting process involving a tetracoordinate sulfurane intermediate. The large value of β_{nuc} that is observed suggests that the buffer-catalyzed reaction involves *O*-acyl sulfoxide formation; the predominant role of the methionyl carboxyl group in the reaction seems to be as an intramolecular deacylation catalyst.

The iodide oxidation of simple sulfides is thought to proceed through the formation of an intermediate iodosulfonium ion which can undergo hydrolysis by the direct addition of solvent to give the corresponding sulfoxide.[1-6] The oxidation reaction is strongly catalyzed by anionic nucleophiles including carboxylate buffers.[1,2,4,5] The mechanism of the carboxylate catalysis is thought to involve the intermediate formation of an *O*-acyl sulfoxide which can undergo uncatalyzed hydrolysis or acyl transfer to a second mole of buffer, giving buffer anhydride and sulfoxide[1,5] (Scheme I). Intramolecular catalysis of the iodine oxidation of sulfides and of the iodide reduction of sulfoxides by carboxylates placed ortho to the sulfur in a benzene ring or two atoms removed in aliphatic systems has been reported and rate enhancements of 10^3–10^4 attributed to this catalysis.[7-10] While this catalysis is certainly real and significant, important questions remain concerning the rate-limiting step in these cases and the actual catalytic efficiency of the intramolecular groups relative to the carboxylate catalysis observed in intermolecular reactions.

We have recently described the mechanism of the carboxylate catalysis in the iodine oxidation of *N*-acetylmethionine methyl ester.[5] In order to define the importance of the intramolecular carboxylate catalysis in these types of oxidation reactions, we have investigated the catalysis of the iodine oxidation of *N*-acetylmethionine by a series of carboxylate buffers.

Scheme I

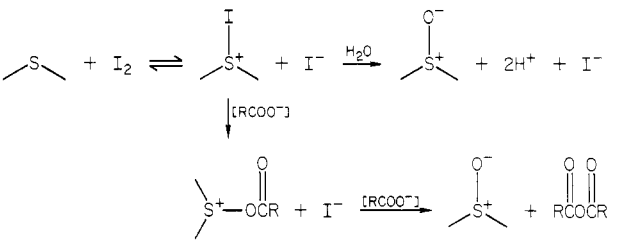

Table I. Apparent Catalytic Constants for Buffer Catalysis of the Iodine Oxidation of *N*-Acetylmethionine [a]

buffer	fraction base	no. of points	k_c, M^{-2} s^{-1} [b]
propionate	0.50	7	40.0
	0.70	7	76.0
	0.80	12	86.0
acetate	0.30	7	15.3
	0.50	4	24.0
	0.60	7	49.3
	0.70	8	56.7
3-chloro-propionate	0.50	7	6.11
	0.70	7	12.8
glycolate	0.50	4	2.7
	0.70	8	3.8
	0.80	6	4.4
chloroacetate	0.70	4	0.56
	0.85	4	0.25
	0.90	4	0.43

[a] Aqueous solution, 25 °C, ionic strength 1.0 with KCl. [b] Apparent catalytic constant for buffer catalysis, obtained obtained from linear slopes of plots of k_{obsd} vs. [buffer].

Experimental Section

Materials. Reagent grade inorganic salts were used without further purification. Organic acids, with the exception of reagent grade acetic acid, were recrystallized or distilled prior to use. Stock solutions of *N*-acetylmethionine were prepared at about 0.1 M in glass distilled water. Iodine stock solutions were 0.1 M in 1 M KI. Reactions were initiated by the addition of a small amount of the iodine solution to preequilibrated cuvettes containing buffer, *N*-acetylmethionine, KI solution, and the required amount of KCl to give an ionic strength of 1.0. Chloride ion did not inhibit the oxidation reaction. Glass distilled water was used throughout; the pH of each cell was measured at the completion of the experiment, using a Corning 130 pH meter equipped with a combined glass electrode.

Kinetic Measurements. The rates of disappearance of I_3^- were followed at 353 nm, using a Hitachi 100-60 spectrophotometer equipped with an automatic cell changer and a thermostated cell compartment. First-order rate constants were determined from

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(10) Allenmark, S. *Acta Chem. Scand.* **1965**, *19*, 1667.

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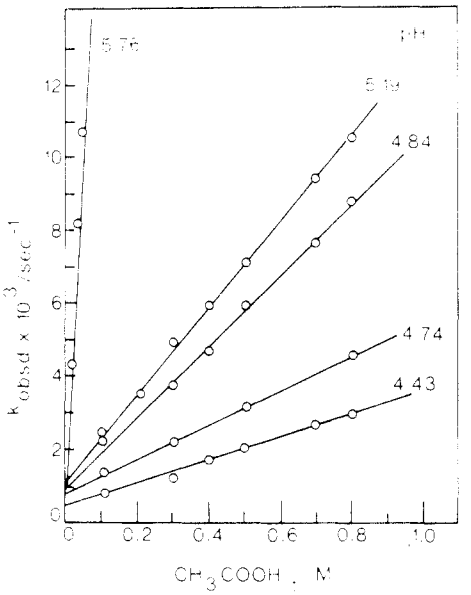


Figure 1. Plot of observed first-order rate constants for the iodine oxidation of *N*-acetylmethionine against the concentration of acetic acid buffers. The fraction of the buffer in the basic form is as follows: pH 4.43, 30%; pH 4.74, 50%; pH 4.84, 60%; pH 5.19, 70%; pH 5.76, 90%. Initial concentrations: [NAM] = 1.67×10^{-3} M, [I_2] = 1.67×10^{-5}, [I^-] = 0.01 M; the ionic strength was 1.0 with KCl, 25 °C.

Table II. Carboxylate Catalysis of the Iodine Oxidation of *N*-Acetylmethionine [a]

buffer	pK_a [b]	K_1k_B, M^{-2} s^{-1} [c]
propionate	4.87	94 ± 14
acetate	4.76	65 ± 18
3-chloropropionate	4.08	15.3 ± 3
glycolate	3.83	5.8 ± 0.2
chloroacetate	2.87	0.5 ± 0.2

[a] Aqueous solution, 25 °C, ionic strength 1.0 with KCl. [b] Thermodynamic pK_a from ref 14. [c] Catalytic constant for buffer catalysis, see Scheme II.

semilogarithmic plots of $A_\infty - A_t$ against time and were typically linear for 3–4 half-times. Constants for buffer catalysis were obtained from the slopes of plots of observed rate constants against buffer concentration. Replots of these slopes against the fraction of the buffer in the basic form were linear for fractions up to 70% base and the catalytic constant for the buffer anion was obtained by extrapolation to 100% base.

The equilibrium constant for the formation of I_3^- is 723 M^{-1}.[5] In experiments in which very low concentrations of iodide were used in order to determine iodide dependence, the concentration of iodide was corrected for I_3^- formation by using this constant.

Results

Rate constants for the iodine oxidation of *N*-acetylmethionine increase linearly with increasing buffer concentrations of carboxylate buffers (Figure 1). Catalytic constants for the various buffer species were obtained by plotting the apparent catalytic constant (k_c, Table I) against the fraction of the buffer in the basic form. Catalytic constants for the five buffers examined are collected in Table II.

Buffer-independent rate constants (k_0) for the uncatalyzed oxidation reaction were obtained by extrapolation of linear buffer plots to zero buffer concentration. These data are plotted as a function of pH in Figure 2; the solid line is calculated for a change in slope of zero to 1, occurring at pH 3.4.

The iodide dependence of the oxidation reaction was determined at both high and low buffer concentrations.

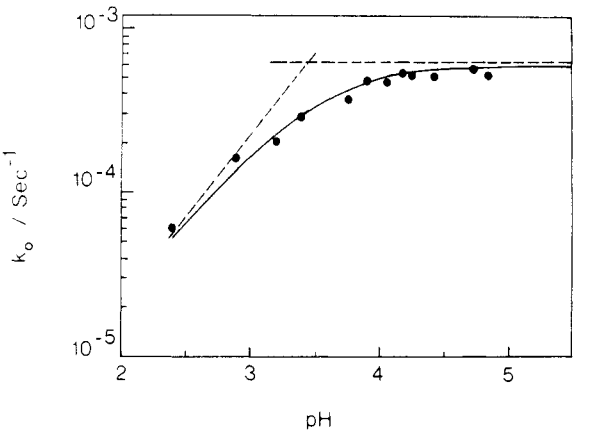


Figure 2. Dependence on pH of the observed first-order rate constants for the iodine oxidation of *N*-acetylmethionine; 25 °C, ionic strength 1.0 with KCl. All data are extrapolated to zero buffer concentration, and the solid line is calculated for an ionization occurring at pH 3.4.

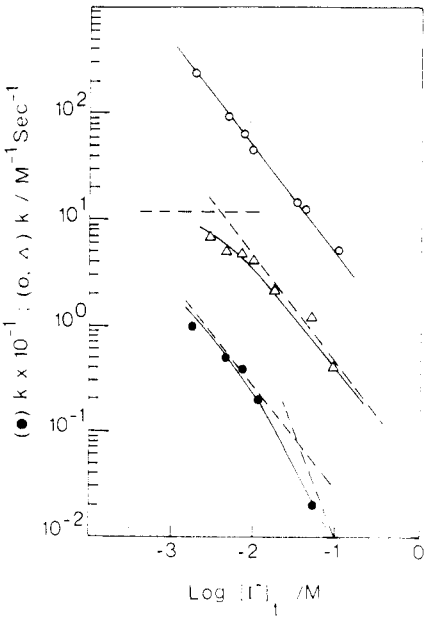


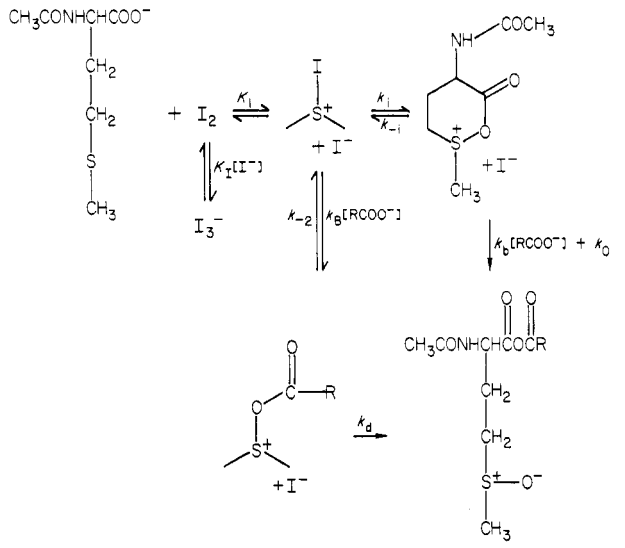
Figure 3. Double logarithmic plot of $k = k_{obsd}[I^-]$ against iodide concentration at the following concentrations of acetic acid buffers: (○) pH 4.61, 0.5 M; (△) pH 4.60, 0.001 M; (●) pH 3.60, 0.001 M. Aqueous solution, 25 °C, ionic strength 1.0 with KCl.

At a concentration of acetate buffer of 0.001 M, pH 4.60, the rate constants are a nonlinear function with respect to iodide concentration, as shown by the double-logarithmic plot in Figure 3. The data in the figure are accommodated by a theoretical curve, breaking from slopes of zero to −1 at an iodide concentration of 0.0025 M. Since the data are plotted as log ($k_{obsd}[I^-]$) vs. log [I^-], the break of zero to −1 would correspond to a change of an inverse to an inverse-squared dependence in the rate law. At very low concentrations of I^-, the equilibrium between I_2 and I^- becomes significant and the total concentration of free I^- was corrected for this equilibrium. At high concentration of acetate buffer (0.5 M, pH 4.61), the iodide dependence is a simple inverse squared. At very low buffer concentration (0.001 M) at pH 3.6, the data tend to curve downward at higher iodide concentration, suggesting a changeover to an inverse-cubed dependence.

Discussion

Rate constants for the iodine oxidation of *N*-acetylmethionine (NAM), extrapolated to zero buffer concen-

Scheme II



tration, are shown in the pH–rate profile in Figure 2. The data are accommodated by a break from slopes of zero to 1, occurring at pH 3.4, essentially identical with the pK_a of 3.44 for the ionization of NAM under the experimental conditions.[12] The observed first-order rate constant for the oxidation of NAM, free base, can be compared with the rate constant for the oxidation of *N*-acetylmethionine methyl ester under the same conditions.[5] At pH 5 and at zero buffer concentration, the rate constant for the uncatalyzed oxidation of the methyl ester is 5.1×10^{-7} s^{-1} at an iodide concentration of 0.01 M and a total ester concentration of 1.67×10^{-3} M; the order with respect to iodide under these conditions is inverse squared.[5] For the oxidation of NAM, also at 0.01 M I^- and 1.67×10^{-3} M *N*-acetylmethionine, free base, the first-order rate constant is 7×10^{-4} s^{-1}; the iodide dependence under these conditions is also inverse squared. The ratio of these two rate constants gives a rate acceleration of slightly less than 1400-fold for the oxidation of *N*-acetylmethionine. Since, on the basis of Figure 2, the reactive form of NAM is the free base, and carboxylate anions are well-known to strongly catalyze the oxidation of simple sulfides by a nucleophilic mechanism,[1,4,5] it is reasonable to suggest that intramolecular catalysis is responsible for the observed rate acceleration. As shown in Scheme II (upper pathway), the initially formed iodosulfonium ion in NAM can be trapped by the rapid formation of a cyclic *O*-acyl sulfoxide which can then undergo hydrolysis to give sulfoxide. The factor of about 1400 in rate acceleration that is observed for this reaction is consistent with the effects of intramolecular carboxylate groups in the iodine oxidation of sulfides and in the iodide reduction of sulfoxides.[7-10] Similar cyclic *O*-acyl sulfoxides have been suggested in these reactions and rate accelerations of 10^3–10^4 have been reported.

While these rate accelerations are interesting, the importance of intramolecular catalysis can be best assessed by comparing the rate constant for the intramolecular reaction with the rate constant for the intermolecular, carboxylate-catalyzed reaction. For the buffer-independent (top) pathway in Scheme II, the observed first-order rate constant is given in eq 1. The fact that an inverse-squared dependence on iodide ion iodide ion is typically observed means that the term $k_{-1}[I^-]$ must dominate the denominator and the equation simplifies to eq 2 (k′ is

$$\frac{k_{obsd}(1 + [H^+]/K_a)}{[NAM]} = \frac{k_1[k_i k_0/(k_{-i}[I^-] + k_0)]}{K_I[I^-][k_{-1}[I^-] + [k_i k_0/(k_{-i}[I^-] + k_0)]]} \quad (1)$$

corrected for [NAM], free base). At higher or lower pH,

$$k'_{obsd} = \frac{K_1 k_i k_0}{K_I[I^-]^2(k_{-i}[I^-] + k_0)} \quad (2)$$

the trends in iodide dependence toward inverse and inverse cubed, respectively (Figure 3), suggests that the term k_0 is base dependent, becoming small at low pH ($k'_{obsd} = K_1 k_i k_0 / K_I k_{-i}[I^-]^3$) and larger at high pH so that $k_{-1}[I^-]$ in eq 1 becomes smaller than k_0 and k'_{obsd} is simply equal to $k_1/K_I[I^-]$.

Since, at 0.01 M iodide, the iodide dependence of the oxidation of NAM approaches inverse squared, the rate-limiting step must occur *before* deacylation (Scheme II). The observed rate is 0.01 M. This can be compared with the catalytic constant for the glycolate-catalyzed (pK_a = 3.75)[14] oxidation of *N*-acetylmethionine methyl ester; the catalytic constant in the region of low buffer concentration is $K_1 k_B / K_I[I^-]^2$, where k_B is the rate constant for the formation of the *O*-acyl sulfoxide.[5] The catalytic constant for this buffer is about 3×10^{-4} M^{-1} s^{-1}, giving a rate advantage for the intramolecular reaction of 2.3 M. If the equilibrium constant for the formation of the iodosulfonium ion is the same for these two methionine derivatives, then the factor of 2.3 M represents the ratio of k_i to k_B for carboxylate anions of roughly comparable pK_a. This intramolecular advantage is very small relative to the large accelerations that one might expect based on entropic considerations. Page and Jencks[15-18] have suggested that the maximum rate acceleration expected for a bimolecular reaction which is effectively converted to a unimolecular reaction by the complete loss of translational, rotational and internal entropies is about 10^8 M. In the cyclization reaction in question, several degrees of freedom remain for rotation around carbon–carbon and carbon–sulfur bonds; nevertheless, an acceleration of about 10^4 M might be anticipated for this particular reaction.[17,18] Very low "effective molarities" such as the 2.3 M observed in the present case are expected in those reactions in which[16,17] (a) a "loose", high-entropy transition state is involved in the rate-limiting step, (b) the intramolecular reaction generates a significant amount of ring strain, or (c) in which the step of the reaction enjoying the intramolecular advantage is not rate limiting.

Although thermodynamic data for this type of oxidation reaction are available in the literature,[4,10] the fact that multiple equilibria are involved, prior to the rate-limiting step, makes the rigorous interpretation of activation entropies impossible. It is doubtful, however, the *O*-acyl sulfoxide formation would proceed through an unusually loose transition state. The fact that β_{nuc} for *O*-acyl sulfoxide formation from *N*-acetylmethionine methyl ester is 1.0[5] suggests that bond formation is quite extensive, implying a highly ordered transition state. Literature ex-

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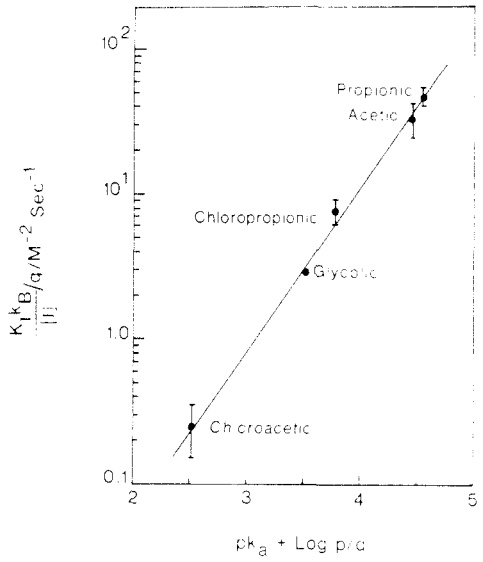


Figure 4. Brønsted plot of catalytic constants for carboxylate catalysis of the iodine oxidation of *N*-acetylmethionine. The solid line is drawn with a slope of β_{nuc} = 1.1.

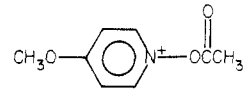
amples of "loose" transition states are most common in those reactions where diffusion or simple proton transfer are rate limiting.[16]

It is also unlikely that the cyclic *O*-acyl sulfoxide shown in Scheme II would be highly strained. Six-membered sulfur heterocycles are relatively strain-free; the strain energy of tetrahydrothiopyran being estimated to be comparable to that for cyclohexane.[17] The inclusion of the acyl moiety in the ring will, no doubt, introduce strain; however, this would probably be small, based on the strain of 5.9 kJ/mol for glutaric anhydride, relative to cyclohexane.[17] It seems unlikely that this small amount of strain energy would result in such a significant hindrance of the intramolecular reaction in the present case.

As mentioned above, a low effective molarity is also expected if the intramolecular reaction is not rate limiting. In the present case, the iodide dependence requires that the rate-limiting step come *before* deacylation. The simplest conclusion would be that ring closure would be rate limiting; however, this is the very step that we would expect to display the *largest* effective molarity. This apparent contradiction would be resolved if an additional intermediate existed between the iodosulfonium ion and the *O*-acyl sulfoxide. Kinetically, this intermediate must have the stoichiometry and charge of a tetracoordinate sulfurane. If a sulfurane is an obligatory intermediate in the carboxylate-catalyzed oxidation reaction, and if the breakdown of the sulfurane is slow, then the same step would be rate limiting in the intra- and intermolecular catalyzed reactions and a small effective molarity would be expected. The fact that such sulfuranes are known to undergo pseudorotation[19,20] raises the interesting possibility that the rate-limiting kinetic process in the intramolecular reaction might be an obligatory pseudorotation, slowed by the cyclic structure but proceeding rapidly in the acyclic compound.

Carboxylate Catalysis. The rate constants for the iodine oxidation of *N*-acetylmethionine are strongly dependent upon the concentration of carboxylate buffers (Figure 1). At constant pH, the first-order rate constants increase as a linear function of buffer concentration for all buffers examined. Catalytic constants for five carboxylic acid buffers are collected in Table II. The pK_a dependence of these catalytic constants is shown in Figure 4; the Brønsted coefficient, based on these data, is β_{nuc} = 1.1.

We have previously shown that for the carboxylate-catalyzed iodine oxidation of *N*-acetylmethionine methyl ester, β_{nuc} for the *O*-acyl sulfoxide forming step was 1.0. In the present case, the enhanced rate of the uncatalyzed oxidation reaction (about 1400-fold) over the uncatalyzed rate for the corresponding methyl ester suggests that the carboxylate anion of NAM is participating in an intramolecular reaction to give the cyclic *O*-acyl sulfoxide (Scheme II). In this mechanism, the linear buffer catalysis that is observed would represent catalysis of the deacylation reaction. However, the value of β_{nuc} that is observed (1.1) is significantly larger than might be expected for a simple nucleophilic deacylation reaction of this type. In general, small values of β_{nuc} are observed whenever the pK_a of the catalyst is significantly larger than the pK_a of the leaving group.[21] In cases such as this, attack at the acyl carbon is generally rate limiting. Consistent with this is the approximate β_{nuc} of $\simeq$0.7 that is observed for the deacylation of 1-acetoxy-4-methoxypyridinium ion (I) by phenolate anions.[21] Phenols, as a group, have an average



I

pK_a that is about 6 units above the pK_a of the leaving group, 4-methoxypyridine 1-oxide (pK_a = 2.05).[14] This is approximately equal to the ΔpK_a between the acetate catalysts and the pK_a of dimethyl sulfoxide (pK_a = −1.54).[22] While it is possible that the cyclic nature of the *O*-acyl sulfoxide results in a change in the rate-limiting step from attack to breakdown of the tetrahedral intermediate, the similarity between the β_{nuc} observed in the present case (1.1) and the β_{nuc} of 1.0 previously observed for *O*-acyl sulfoxide *formation*[5] suggests that this step might also be rate limiting in the present case. This suggestion would also be consistent with the very small effective molarity that is observed for the intramolecular carboxylate of NAM.

Since linear catalysis is observed in the oxidation of NAM and nonlinear, second-order catalysis is observed in the oxidation of the corresponding methyl ester, the intramolecular carboxylate must have *some* role in the buffer-mediated reaction. We suggest that the major role may be as an effective intramolecular *deacylation* catalyst. Higuchi and co-workers have reported that dicarboxylate anions are extremely effective catalysts for the iodine oxidation of simple sulfides.[1] In their pioneering studies they observed that the reaction was first order with respect to buffer and that carboxylate anhydride was produced during the oxidation reaction.[1] The mechanism suggested involves the formation of an *O*-acyl sulfoxide which rapidly undergoes internal deacylation. For *N*-acetylmethionine, the intramolecular carboxylate anion, while a poor nucleophile for the intramolecular *O*-acyl sulfoxide formation, would seem to be an entirely adequate catalyst for the intramolecular deacylation reaction. The fact that acetate buffer, 90% base (Figure 1), is *more* efficient as a catalyst than would be predicted based on the data at lower fractions of base, suggests that the intermolecular deacylation

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(20) Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 2895.
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reaction is beginning to compete with the intramolecular reaction.

Conclusion. The carboxylate catalysis of the iodine oxidation of *N*-acetylmethionine seems to involve an *inter*molecular reaction to give an intermediate *O*-acyl sulfoxide which is rapidly deacylated by reaction with the *intra*molecular carboxylate. Intramolecular *O*-acyl sulfoxide formation seems to be unfavorable, or does not rapidly lead to products, and is observed only in the buffer-independent reactions.

Acknowledgment. This work was supported by Grant CHE-8000054 from the National Science Foundation.

Registry No. *N*-Acetylmethionine, 65-82-7; I_2, 7553-56-2.

Synthesis of New Functional Acenaphthylene Derivatives. 2. Regioselective Electrophilic Substitution of Silylated Acenaphthenes and Acenaphthylenes

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Received July 29, 1981

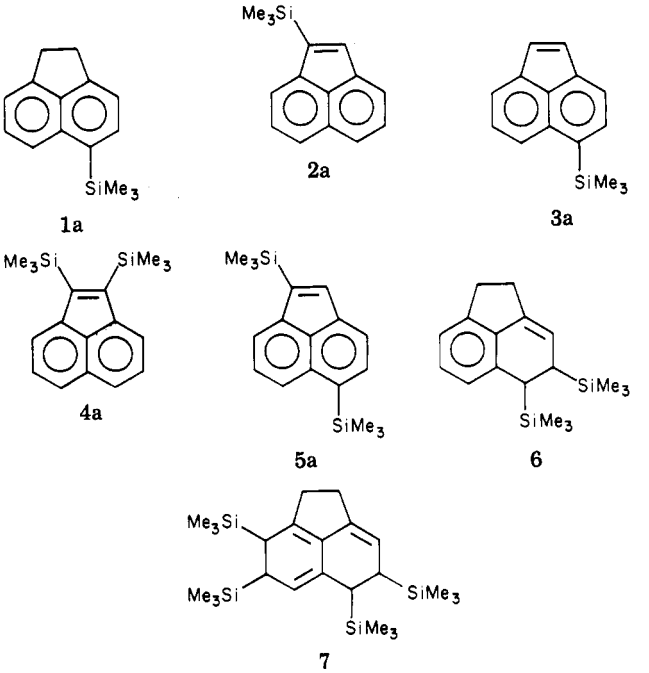
New silylated derivatives have been synthesized in the acenaphthylene series [5-(trimethylsilyl)acenaphthene (**1a**) and -acenaphthylene (**3a**), 4,5-bis(trimethylsilyl)-4,5-dihydroacenaphthene (**6**), and 4,5,7,8-tetrakis(trimethylsilyl)-4,5,7,8-tetrahydroacenaphthene (**7**)] by appropriate silylation reactions, followed by oxidation in the case of **3a**. **1a** and **3a** as well as 1-(trimethylsilyl)- and 1,2- and 1,5-bis(trimethylsilyl)acenaphthylenes (**2a**, **4a**, and **5a**, respectively) have been used as regioselective precursors of 5-functional acenaphthenes and 1-monofunctional and 1,2- and 1,5-bifunctional acenaphthylenes by electrophilic substitution of the trimethylsilyl group(s). Mono- and bisulfonations succeeded in all cases as well as the acylation or iodination of monosilyl derivatives and 1,2-diodination of **4a**. Thus, various novel functional acenaphthenes and acenaphthylenes could be prepared by a convenient route. In contrast, attempts at diodination of **5a** and diacylation of **4a** and **5a** were unsuccessful.

In a previous paper[1] we have described the synthesis of various trimethylsilyl- or bis(trimethylsilyl)acenaphthenes and acenaphthylenes (e.g., **2a**, **4a**, and **5a**; Chart I).

We have now focused our interest on the functionalization of these compounds by regioselective substitution of the trimethylsilyl group(s) because very few of functional acenaphthylene derivatives have been described to date.[2] We thought the silicon route would be applicable to that purpose in view of previous results on the electrophilic substitution of vinyl[3] and arylsilanes,[4] especially in studies in our laboratories.

Reductive silylation of acenaphthene by magnesium in hexamethylphosphortriamide (HMPA)[5] in the presence of trimethylchlorosilane led to 4,5-bis(trimethylsilyl)-4,5-dihydroacenaphthene (**6**,[1] Scheme I). Using lithium with THF as the solvent,[5-7] 4,5,7,8-tetrakis(trimethylsilyl)-4,5,7,8-tetrahydroacenaphthene (**7**), the first product having the 4,5,7,8-tetrahydronaphthalene structure, was

Chart I



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