definitively ruled out. For this reason, we have presented both s-cis and s-trans models in Figure 2.

Summary

The models illustrated in Figure 2a,b for the chromophore and its protein environment in bR are the ones that optimally fit both the dihydro and all the ^{13}C NMR data. The essential features of these model are (1) a weak counterion to reproduce the large opsin shift of 7,8-dihydro-bR, (2) a negative charge near C5 to reproduce the opsin shift of the bR and the large downfield chemical shift of C5 relative to PRSB, (3) a positive charge near C7 to depress the opsin shift of 5,6-dihydro-bR relative to 7,8-dihydro-bR and native bR and to account for the upfield chemical shift of C7 in bR relative to PRSB, and (4) a ring-chain conformation that has a ring methyl in contact with the hydrogen on C8 to produce a γ effect on C8, accounting for its large upfield chemical shift. Both the s-cis and the s-trans configurations about the ring produce excellent agreement with the experimental data.

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Registry No. *all-trans*-RET, 116-31-4; 5,6-H_2-RET, 11907-28-9; 7,8-H_2-RET, 75917-44-1; 9,10-H_2-RET, 72535-17-2.

Bacterial Organomercurial Lyase: Novel Enzymatic Protonolysis of Organostannanes†

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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received March 10, 1987*

Abstract: Pure bacterial organomercurial lyase has been found to catalyze a protonolytic cleavage of the carbon-tin bond in certain organostannanes. Of the compounds tested tetravinyltin is turned over with the highest specific activity, yielding ethylene as the organic product. Similarly, triethylvinyltin undergoes turnover by the lyase to yield ethylene and ethane in a 97:3 ratio, at $^1/_{60}$th the rate of tetravinyltin turnover. Finally, tetramethyltin and trimethyltin fluoride yield small amounts of methane (2-5 turnovers/mol of enzyme) prior to eventual loss of enzyme activity. The decrease in activity observed during turnover of the organostannanes is consistent with the observed inhibition of the enzyme by dimethyltin dibromide.

Bacterial organomercurial lyase catalyzes a remarkable protonolytic cleavage of the carbon-mercury bond in organomercurials.[1] This reaction constitutes the first detoxification step of the "broad spectrum" bacterial mercury resistance pathway, yielding inorganic Hg(II) and the corresponding hydrocarbon RH (Scheme I). The detoxification sequence is completed in a second step by the flavoenzyme mercuric reductase, which effects reduction of Hg(II) to Hg(0). The Hg(0) subsequently evaporates from the cellular microenvironment, thereby completing removal of the mercury. Recent reports from this laboratory have described purification of these two enzymes and elucidation of the mechanisms by which they carry out their transformations.[2,3]

The widespread use of organometallic compounds as antimicrobial agents and the resulting ubiquitous environmental distribution of these compounds are well documented.[4,5] Organomercurials have found extensive use as bactericides, fungicides, and slimicides, and a range of organostannanes have been developed for use as marine antifouling agents, wood preservatives, polymer stabilizers, germicides, and fungicides. Mechanisms for microbial resistance to these compounds have evolved[6-10] and constitute a challenge to the development of new organometal-based antimicrobials. While the details of microbial degradation of organomercurials are fairly well understood, less is known about the corresponding degradation of organostannanes. For example, bacterial and fungal degradation of tributyltin oxide to give mono- and dibutyltin compounds has been noted, although the mechanism of this degradation has not been determined.[9,10]

In order to test our hypothesis that the enzymatic C-Hg bond cleavage that confers bacterial resistance to organomercurials may be paradigmatic for microbial detoxification of other organometallic compounds, we have screened a number of compounds possessing a carbon-metal bond as substrates for pure organomercurial lyase. We report here our finding that certain organostannanes are indeed substrates for the lyase, resulting in an apparent protonolytic cleavage of the carbon-metal bond. The specificity of the enzyme for organostannanes is significantly

Scheme I

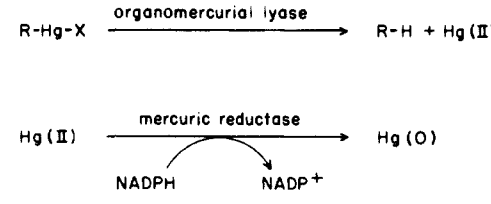

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Table I. Turnover of Organostannanes by Organomercurial Lyase[a]

entry	substrate	K_m, mM	V_{max}, nmol/min per mg	turnover no.	turnovers/mol of enzyme
1	$Sn(CH{=}CH_2)_4$	0.5[b]	9.0	0.2 min^{-1}	many[d]
2	$Et_3Sn(CH{=}CH_2)$	1.0[b]	0.15	0.2 h^{-1}	many[e]
3	Me_4Sn	*c*	*c*	*c*	5.5[f]
4	Me_3SnF	*c*	*c*	*c*	2.4[f]

[a] Kinetic parameters were measured as described under Methods. [b] Substrate inhibition observed above 1.0 mM. [c] Not determined. [d] The sole gaseous product was ethylene. [e] The gaseous product was ethylene/ethane (97:3). [f] This number is the total hydrocarbon quantity produced before turnover ceases.

narrower than for organomercurials, however, and the organostannanes that are substrates possess lower V/K values than organomercurials. These factors limit the range of mechanistic experiments and kinetic data available for organostannanes. The finding that an enzymatic protonolysis of organostannanes can in fact occur, however, suggests that an enzyme similar to organomercurial lyase that is optimized for organostannane cleavage may exist in nature as part of the microbial resistance pathway to these compounds.

Experimental Section

Materials. Organomercurial lyase was obtained from fermentation of *Escherichia coli* JM101 (pT7-4B, pGP1-2) and purified to homogeneity according to the procedure described previously.[2a] Tetramethylsilane was obtained from Aldrich Chemical Co., tetravinyltin was a gift from Professor William R. Roush, and all other organometallic compounds were provided by the research group of Professor D. Seyferth. Tetravinyltin and triethylvinyltin were redistilled prior to use in kinetic analyses.

Methods. Assay Procedure. The organometallic compound (5–10 μL of a 0.1 M solution in dimethyl sulfoxide or ethanol, final 0.5–1.0 mM concentration) was added to the assay buffer (1 mL; 50 mM NaP_i, 5 mM cysteine, pH 7.4) containing organomercurial lyase (30–60 μg, 1.3–2.7 nmol) in a sealable Wheaton vial. Mercuric reductase and NADPH were present as described for the assay of organomercurials,[2a] although control experiments later indicated that they were not required for activity. The vial was sealed and heated at 37 °C. Activity was followed by monitoring hydrocarbon production via gas chromatography. Aliquots of the reaction headspace (50 μL; $^1/_{80}$th of headspace volume) were injected onto a 80% Porapak N/20% Porapak Q column (0.25 in. × 8 ft) operating at 130 °C. The hydrocarbon products were identified by coinjection of the reaction headspace with standard samples. Total turnover numbers were determined by quantitative analysis of the gaseous products via calibration with known standards.

Kinetic Parameters. Kinetic parameters for the turnover of tetravinyltin and triethylvinyltin were determined by measuring the rate of ethylene formation at 0.1–0.5 mM concentrations of substrate. Data for concentrations outside of this range could not be obtained due to substrate inhibition at high concentrations and insufficient hydrocarbon production for accurate analysis at low concentrations.

Inhibition Experiments. Analysis of inhibition of organomercurial lyase was performed by initiating turnover of either ethyl- or vinylmercuric bromide (0.5 mM) with the enzyme (2.5 μM) according to the general assay procedure. When a linear rate was obtained (ca. 16–17 min), the putative inhibitor was added to the assay mixture and the resultant activity (ethane or ethylene production) was monitored.

Results

Organometal compounds were tested as potential substrates for organomercurial lyase by using the standardized assay procedure described in the Experimental Section. Activity was monitored by direct analysis of the reaction headspace for the expected hydrocarbon product via gas chromatography. This assay was similar to that used previously for the assay of enzymatic protonolysis of organomercurials.[2] For each compound control experiments were carried out with all assay components except for the lyase present.

A number of organometal compounds were considered as possible substrates for the lyase. In practice, however, the choice of substrates was limited to compounds that possessed adequate protonolytic stability toward the aqueous buffer system employed in the assay. This effectively eliminated allyl- and phenylmetal compounds (e.g., tetraallyltin, tetraphenyltin) from consideration, although the allyl- and phenylmercurials are stable in the buffer and are excellent substrates for the enzyme. We thus focused our attention on the known and readily available stable alkyl and vinyl derivatives of tin, silicon, and germanium.

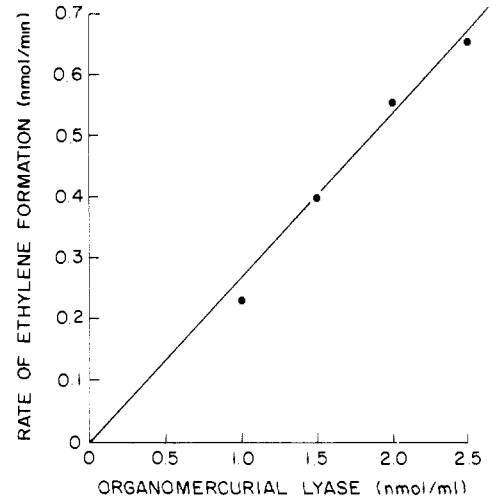


Figure 1. Plot of V vs [E] for protonolysis of tetravinyltin by organomercurial lyase. Rates were determined with the assay procedure described in Methods. The concentration of tetravinyltin in these experiments was 0.5 mM.

Results from the screening of organometal compounds as substrates for organomercurial lyase are presented in Table I. Of particular interest is the finding that certain organostannanes including tetravinyltin, triethylvinyltin, tetramethyltin, and trimethyltin fluoride are substrates for the lyase. No activity was observed, however, with the corresponding alkyl and vinyl derivatives of silicon and germanium (tetravinylsilane, tetramethylsilane, tetravinylgermane, triethylvinylgermane, and tetramethylgermane). Other stannanes, including tetraethyltin, tetrabutyltin, triethyltin acetate, tributyltin oxide, dimethyltin dibromide, and monobutyltin trichloride, likewise were not substrates for the lyase.

Hydrocarbon products from the organostannane protonolyses were identified and quantified by comparison with authentic standards via gas chromatography on an 80% Porapak N/20% Porapak Q column (0.25 in. × 8 ft; 130 °C) designed to separate low molecular weight hydrocarbons. A velocity versus enzyme concentration plot for the protonolysis of tetravinyltin confirmed that ethylene is produced enzymatically (Figure 1). Curiously, the turnover of tetravinyltin did not require a buffer thiol (cysteine) while turnover of the methyltin compounds was dependent on thiol, a strict requirement for organomercurial turnover.[2] The reason for this dichotomy is not readily apparent. In the case of organomercurial protonolysis we postulated that a buffer thiol was necessary for removal of Hg(II) from the enzyme active site; perhaps the vinylstannane protonolysis products can be removed from the active site by water or phosphate, while the methylstannane product requires a thiol for decomplexation.

Analyses of the four compounds showing activity with the lyase indicated that while methane formation could be detected from tetramethyltin and trimethyltin fluoride, the turnover rates were too low for accurate analysis (Table I). Turnover of tetravinyl- and triethylvinyltin was sufficiently rapid, however, to allow kinetic analysis. Tetravinyltin is cleaved with saturation kinetics; K_m = 0.5 mM with V_{max} = 9.0 nmol/min per mg (0.2 turnovers/min). This turnover rate is approximately one-third that of methyl-

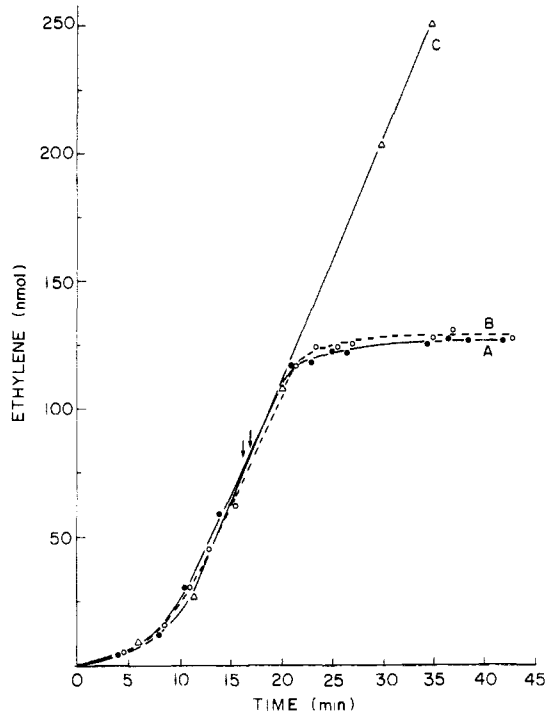


Figure 2. Demonstration of inhibition of organomercurial lyase by dimethyltin dibromide and triethyltin acetate. These experiments were performed as described in Methods. The arrows indicate the time at which the organostannane was added: curve A (●); dimethyltin dibromide added (2.5 μM final concentration); curve B (○); triethyltin acetate added (500 μM final concentration); curve C (△), control (no inhibitor added).

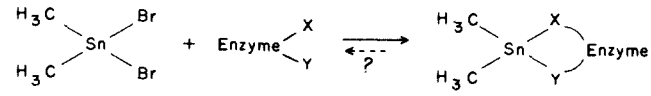
mercuric chloride (31 nmol/min per mg, with K_m = 0.5 mM), itself one of the slowest organomercurial substrates. Cleavage of triethylvinyltin proceeded at approximately $^1/_{60}$th the rate for tetravinyltin protonolysis, with K_m = 1.0 mM and V_{max} = 0.15 nmol/min per mg (0.2 turnover/h). Careful GC analysis of the hydrocarbon product from triethylvinyltin revealed that ethylene and ethane were produced in a ratio of 97:3. Although no activity was observed within the limits of detection with tetraethyltin or triethyltin acetate, these results indicate that cleavage of an ethyl–tin bond can occur, albeit at an almost undetectable rate.[11] During enzymatic cleavage of the organotin compounds a consistent, significant falloff of enzyme activity was observed after ca. 30 min, suggesting possible product inhibition by the putative tri- and/or diorganotin protonolysis products. This hypothesis was quickly tested with several di- and trisubstituted tin species.[12]

Typical inhibition experiments proceeded by initiating enzymatic reaction with a suitable organomercurial substrate (ethylmercuric chloride or vinylmercuric bromide) and measuring the reaction rate (to ethane or ethylene, respectively). The putative inhibitor was then added, and the subsequent rate of organomercurial turnover was monitored. Di- and trialkyltin compounds were both observed to inhibit the enzyme (Figure 2). Of particular note is the potent inhibition of the lyase by dimethyltin dibromide. Enzyme activity was in fact lost after ca. 15 min at virtually equimolar ratios of dimethyltin dibromide to enzyme (2.5 μM each). Treatment of the lyase with dimethyltin dibromide followed by gel filtration or dialysis to remove the reagent resulted in only 9% of the original activity, suggesting that irreversible inhibition had occurred. Enzyme activity was not restored by treatment with thiols. Curiously, there is specificity for the dialkytin counterion; dimethyltin dichloride displays significantly weaker inhibition than the dibromide.

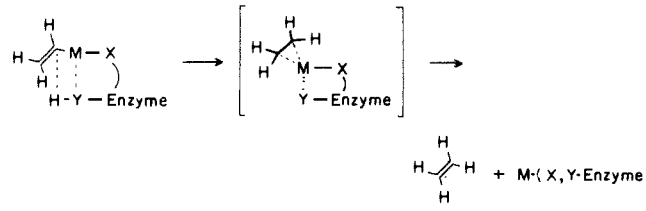
(11) Presumably the small quantity of ethane (3%) observed during turnover of triethylvinyltin arises from cleavage of the ethyl–tin bond. Experiments to rule out alternative possibilities (e.g., from ethylene via a radical mechanism) have not, however, been carried out.

(12) Attempts were made to examine possible substrate inhibition by tetravinyltin and triethylvinyltin and product inhibition by the putative tri-, di-, and/or monovinyltin protonolysis products. These experiments proved to be unfeasible since the vinyltin compounds effect transmetalation of the organomercurials used in the assay. Thus, when tetravinyltin and methylmercuric chloride are each present in the assay mixture, ethylene is formed at a rate similar to that for vinylmercurials.

Scheme II



Scheme III



Discussion

Mechanistic studies on the protonolytic cleavage of acid- and base-stable carbon–mercury bonds by organomercurial lyase indicated that a wide range of organomercurials were substrates for the enzyme. This broad substrate specificity, coupled with relatively high V_{max} values for the reaction, set the stage for a detailed mechanistic study of the enzymatic protonolysis. The presence of a radical pathway was eliminated as a possibility on the basis of specific experiments that probed for intervening radical intermediates. On the basis of our kinetic and stereochemical experiments with a range of specific mechanistic probes we concluded that the reaction most likely proceeds via an S_E2 pathway; the first example of an enzymatic reaction of this type.

In light of the importance of the lyase in microbial detoxification of organomercurials via catalysis of a chemically demanding reaction we questioned whether other organometallic compounds might not be substrates for the enzyme. In practice the range of compounds that could be considered as substrates was limited to those possessing adequate stability in the assay buffer. Alkyl and vinyl derivatives of tin, germanium, and silicon were sufficiently inert to the buffer, while allyl and phenyl derivatives (e.g., allyltributyltin, tetraallyltin, allyltrimethylsilane, allyltriphenyllead) were cleaved too rapidly by the buffer to allow analysis with the enzyme.

The results of this study reveal that in fact certain organostannanes are substrates for organomercurial lyase. Tetravinyltin possessed the highest activity of the compounds tested, with a V_{max} of 9.0 nmol/min per mg and K_m = 0.5 mM (V/K = 18 μL/min per mg). Triethylvinyltin was also processed by the enzyme (K_m = 1.0 mM; V_{max} = 0.15 nmol/min per mg; V/K = 0.15 μL/min per mg), resulting in formation of ethylene and ethane (97:3) as the organic products. The V/K values for tetravinyl- and triethylvinyltin of 18 and 0.15, respectively, compare with values ranging from 60 to 3200 μL/min per mg for organomercurials. Incubation of tetramethyltin and trimethyltin fluoride with the lyase resulted in formation of small amounts of methane, although at rates too slow for kinetic analysis. None of the other stable silicon, germanium, and tin compounds tested showed any hydrocarbon formation upon incubation with the lyase.

During turnover of the tin derivatives a consistent falloff of activity was observed as the reaction proceeded. We speculated that the putative tri-, and di-, and/or monosubstituted tin products of the protonolysis may function as inhibitors of the enzyme. This speculation was confirmed by testing for inhibition by di- and trisubstituted tin compounds. In the event, dimethyltin dibromide functioned as a potent irreversible inhibitor of the lyase. Inhibition by triethyltin acetate indicated that the enzyme was sensitive to inhibition by the trialkyl as well as the dialkylstannane products of protonolysis. Further experiments indicated that dimethyltin dichloride did not display the potent irreversible inhibition of the dibromide, although some inhibition was evident. This may reflect the greater ease of displacement of bromide from tin by enzymic

groups to yield a kinetically inert dialkytin-enzyme substitution complex (Scheme II).[13] We have not completed a detailed kinetic analysis of the inhibition of the enzyme by these various organostannanes.

Previous studies have shown that the relative ease of protonolysis of organostannanes by protic acids (e.g., acetic or hydrochloric acid) is dependent on the organic moiety and decreases in the order vinyl > methyl > ethyl > butyl.[14] This pattern is apparently mimicked in the enzymatic cleavage, where tetravinyltin is cleaved more rapidly than tetramethyltin, and the butyl derivatives are not cleaved at all. Electrophilic reactions of unsaturated organometallics are known to be facilitated via stabilization of the developing positive charge by the metal atom (Scheme III).[15] This stabilization, which was invoked to explain the rate acceleration observed with alkenylmercurials,[2b] may also account for the increased rate of enzymatic cleavage of the vinylstannanes relative to the methyl derivatives. We previously suggested that turnover of organomercurials may involve labilization of the carbon-mercury bond via coordination of an active-site nucleophile to the metal, with concomitant S_E2-type protonolytic bond cleavage. In the present examples of protonolytic cleavage of fully substituted tetraorganostannanes this coordinative labilization presumably cannot occur and may account for the decreased rate of carbon-tin bond cleavage relative to that of carbon-mercury bonds. It is nevertheless noteworthy that cleavage of a vinyl-tin bond, which chemically is carried out by using forcing conditions (glacial acetic acid, 100 °C, 1.5 h for triethylvinyltin),[14] can be effected by organomercurial lyase at a lower temperature (37 °C) and pH 7.4.

Electrophilic reactions of tetrasubstituted organotin compounds are well-known and generally proceed via an S_E2 mechanism.[16] On the basis of this known chemistry and our mechanistic findings on the enzymic cleavage of mercurials it is plausible that the enzymic turnover of the organostannanes reported here may also proceed via an S_E2 pathway. Although the possibility of a radical mechanism cannot be discounted, it appears unlikely given the lack of evidence for a radical pathway in the cleavage of organomercurials.

The turnover of certain organotin compounds by organomercurial lyase is significant in light of the environmental presence of organotin compounds.[4,5] Several reports have presented evidence of microbial resistance to organostannanes,[4-10] although no protonolytic enzymes involved in detoxification have yet been isolated. It appears unlikely that organomercurial lyase per se could confer substantial resistance to organostannanes, given the sluggish V_{max} values and limited range of compounds that are substrates. The existence of organomercurial lyase for detoxification of organomercurials and our observations that certain organostannanes are substrates for it suggest, however, that an analogous enzyme optimized for carbon-tin bond cleavage may exist as a detoxification enzyme of organostannanes.

Finally, the potent inhibition observed with dimethyltin dibromide suggests the possibility of using the tin atom as a tool for probing the active site of organomercurial lyase. The inhibition of numerous enzymes by triethyltin compounds is well-known,[17] as is the inhibition of α-keto acid oxidases by diethyltin dichloride, which is proposed to involve binding of diethyltin to an enzyme dithiol.[18] Elucidation of the intimate mechanistic details of the enzymic cleavage of both organomercurials and organostannanes awaits determination of the active-site sequence and geometry of the lyase, an effort in which the use of organotin inhibitors may prove valuable.

Acknowledgment. Partial support for this research from the National Institutes of Health (Grant GM-20011) is gratefully acknowledged. We thank the research group of Professor D. Seyferth (MIT) for generously providing several of the organometallic compounds described herein, as well as for helpful comments and discussions during the course of this work.

Registry No. $Sn(CH=CH_2)_4$, 1112-56-7; $Et_3Sn(CH=CH_2)$, 2117-47-7; Me_4Sn, 594-27-4; Me_3SnF, 420-60-0; organomercurial lyase, 72560-99-7.

(13) The formation of radicals is expected to be more facile from dimethyltin dibromide than from dimethyltin dichloride. It is thus possible that the differential inhibition observed for the dibromide versus the dichloride is due to a radical mechanism. Experiments to rule out this possibility have not been undertaken.

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Model Reactions Related to Cytochrome P-450. Effects of Alkene Structure on the Rates of Epoxide Formation

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Abstract: A kinetic method for measuring the relative rates of epoxidation of various alkenes, based upon the disappearance of the reactive alkenes carotene or 1,4-diphenylbutadiene, has been developed. With this technique a linear relationship between the logarithm of the rates of epoxide formation and the ionization potential of the alkene has been observed. This contrasts the behavior of peracid epoxidation and provides further evidence for the intermediacy of alkene cation radicals in the hemin-catalyzed epoxidation.

Recent studies of hemin-catalyzed epoxidation of alkenes, model reactions for the function of cytochrome P-450, have employed iron(III) porphyrins and oxidants such as peracids, hydroperoxides, hypochlorite, and iodosylbenzenes.[1-3] These investigations have established that the reaction proceeds through a two-electron-oxidized iron porphyrin, the oxoiron(IV) porphyrin cation radical,[4,5] and that the epoxidation is usually stereospecific.[3,6]

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