

Figure 3. Plot of ΔG^\ddagger (373.15 K) as a function of mole fraction of water in water-dioxane mixtures. Data used was taken from (●) this work¹⁹ and (▲) ref 5.

gether, these results provide very strong evidence that chemical reaction is rate controlling.

With a rate-limiting chemical reaction, the linear dependence of k_0 on surface area shown in Figure 1 can be rationalized only in terms of an interfacial process. Moreover, the fact that this plot extrapolates through the origin shows that the observed reaction takes place exclusively at the phase boundary. Independent evidence that reaction is not occurring in the bulk liquid phases comes from two additional sets of experiments. First, we have found a linear dependence of ΔG^\ddagger on the mole fraction of water present for the hydrolysis of 1-bromoadamantane carried out in homogeneous dioxane-water mixtures (Figure 3). The extrapolated free energy of activation in pure water ($\Delta G^\ddagger = 23.0 \text{ kcal mol}^{-1}$) is considerably lower than that observed for the biphasic process.¹⁸ Second, when a toluene solution of 1-bromoadamantane was saturated with water at 100 °C for 1 h and then heated for another 24 h at the same temperature in the absence of the aqueous layer, no further hydrolysis could be detected.

If Figure 3 is used as a crude calibration to estimate the nature of the microenvironment at the toluene-water interface, an ionizing power equivalent to a 91% (v/v) dioxane-water mixture is obtained. Menger has proposed that a hydrocarbon-water interface is a three-dimensional region containing both hydrocarbon and water which gradually changes into bulk aqueous and organic phases.³ Our data indicate that the toluene-water interface is of intermediate polarity and is consistent with such a model. However, more information is clearly needed before a complete description of the microenvironment is possible.

We believe that biphasic hydrolysis of 1-bromoadamantane represents an attractive kinetic probe for exploring aqueous-organic interfaces and related studies aimed at defining these regions in greater detail are being planned.

References and Notes

- (1) Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG-77-S-02-4446) and the Army Research Office (Contract DAAG-29-76-G-0330).
- (2) Menger³ and Tomita et al.⁴ have reported hydrolysis studies of certain esters carried out as aqueous-organic phase reactions. Although strong evidence for chemical reaction occurring at the interface was presented, the rate-limiting process in both systems appears to be diffusion.
- (3) F. M. Menger, *J. Am. Chem. Soc.*, **92**, 5965 (1970).
- (4) A. Tomita, N. Ebina, and Y. Tamai, *J. Am. Chem. Soc.*, **99**, 5725 (1977).
- (5) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5977 (1970).
- (6) R. P. Bell, *J. Phys. Chem.*, **32**, 882 (1928).
- (7) These experiments were carried out in a 100-mL round-bottomed flask equipped with a sampling port and a Teflon stirring paddle attached to a stirring rod using 25 mL of a 0.01 M solution of 1-bromoadamantane in toluene and 25 mL of 0.1 M aqueous sodium hydroxide. The reaction temperature was 90 °C.
- (8) B. G. Levich, "Physicochemical Hydrodynamics", Prentice-Hall, Englewood Cliffs, N.J., 1962, Chapter 3.
- (9) Observed first-order rate constants were found to be insensitive to both pH (1-13) and concentration of sodium bromide (0.05-1.0 M) in the aqueous phase and to the presence of a surfactant, sodium laurate (5×10^{-5} to 1×10^{-2} M).
- (10) Analysis (GLC) was carried out on a Hewlett-Packard 5830 flame ionization instrument using a 2 ft \times 0.125 in. UC-W982 on Chromosorb W column at 120 °C. The only product found was 1-hydroxyadamantane.
- (11) All kinetic experiments have been performed at least in duplicate; the rate constants given are average values.
- (12) The following culture tube specifications and reaction conditions were used (type of tube; interfacial area (cm²); volume of the organic phase (cm³); volume of the aqueous phase (cm³): A, Corning No. 9826, 13 \times 100 mm; 1.26; 1; 2; B, Corning No. 9825, 20 \times 125 mm; 2.83; 2; 5; C, Corning No. 9825, 25 \times 150 mm; 4.16; 5; 10; D, Kimax No. 45066, 38 \times 200 mm; 9.08; 10; 75. For type A and B tubes, the meniscus was taken into account and computation of the interfacial areas was done using the following equation: $Q = 2\pi rh$, where Q = lateral area of a segment of a sphere, r = radius of the sphere, and h = height of the meniscus. For type C and D tubes the interfacial area is simply the cross section of the tube.
- (13) First-order rate constants, k_{obsd} , were determined by following the decrease in concentration of 1-bromoadamantane in the bulk organic phase as a function of time. For an interfacial reaction, as the ratio, volume of organic phase/surface area, increases the observed rate constant must decrease proportionally.
- (14) Rate constants measured at 95, 100, 105, 110 and 120 °C were 1.20, 1.85, 3.16, 4.76, and $13.36 \times 10^{-6} \text{ s}^{-1}$, respectively.
- (15) 1-Methoxyadamantane was chosen instead of 1-bromoadamantane for this diffusion experiment in order to avoid ambiguities derived from the presence of a second tritiated species, 1-hydroxyadamantane, formed from interfacial and bulk aqueous phase hydrolysis.
- (16) 1-Bromoadamantane was tritiated by exposure to tritium gas (New England Nuclear, Boston, Mass.) and was purified twice by sublimation at 90 °C (1 mm). The specific activity was 2.7 mCi/mg. The radioactive halide was then converted into the corresponding methyl ether using established procedures: P. H. Owens, G. J. Gleicher, and L. M. Smith, Jr., *J. Am. Chem. Soc.*, **90**, 4122 (1968).
- (17) The diffusion experiments were conducted in a modified culture tube (Kimax No. 45066, 38 \times 200 mm). Aliquots of the aqueous layer were withdrawn through a side tube capped with a No-air stopper. Typically, 5- μ L samples were taken and blended with 2 mL of a scintillation liquid. Radioactivity was measured using a Packard Tri-Carb Model 3330 scintillation spectrometer. The counting liquid (Bray's solution) was prepared from 60 g of naphthalene, 4 g of 2,5-diphenyloxazole (PPO), 0.2 g of 2,2'-*p*-phenylenebis(5-phenyloxazole) (POPOP), 100 mL of absolute methanol, 20 mL of ethylene glycol, and 880 mL of scintillation grade dioxane. The concentration of the tritiated 1-methoxyadamantane in water was computed using a standard curve.
- (18) Although hydrolysis in the bulk water phase has a significantly lower free energy of activation, it is clearly not the major reaction pathway. This must be the result of unfavorable partitioning of 1-bromoadamantane in the aqueous phase. Unfortunately, the relative instability of 1-bromoadamantane in water prevents a determination of the distribution coefficient (the half-life of the organic halide in water at 40 °C ($\Delta G^\ddagger = 23 \text{ kcal mol}^{-1}$) is only 20 min).
- (19) These experiments were conducted in 8-mL culture tubes (Corning No. 9826, 13 \times 100 mm) using 2 mL of 0.01 M 1-bromoadamantane in 88 and 92% (v/v) dioxane-water mixtures. First-order rate constants measured at 100, 110, and 120 °C were 0.96, 2.24, and $4.54 \times 10^{-6} \text{ s}^{-1}$ (88%) and 1.28, 2.92, and $6.35 \times 10^{-6} \text{ s}^{-1}$ (92%).

Steven L. Regen,* Jacques J. Besse

Department of Chemistry, Marquette University
Milwaukee, Wisconsin 53233

Received June 2, 1978

Synthesis and Thermal Decomposition of Homoleptic *tert*-Butyl Lanthanide Complexes¹

Sir:

The organometallic chemistry of the lanthanide elements is of interest because the unique physical characteristics which distinguish the lanthanides from other metals may lead to patterns of reactivity for organic molecules attached to the lanthanide center which are substantially different from those found with other metals. Despite this potential for unusual organometallic chemistry, relatively few investigations of the organometallic chemistry of these elements have been made.² We report here the synthesis of a new class of stable, σ -bonded organolanthanide complexes involving the *tert*-butyl ligand:

$\text{LiLn}(t\text{-C}_4\text{H}_9)_4(\text{THF})_x$ ($\text{Ln} = \text{Sm}, \text{Er}, x = 4; \text{Ln} = \text{Yb}, x = 3$; THF = tetrahydrofuran). This class of compounds not only expands the list of available σ -bonded organolanthanides, but also represents only the second example of a homoleptic *tert*-butyl complex.³ In addition, this class provides a unique opportunity to assess the importance of β -hydride elimination in organolanthanide chemistry and to further delineate the differences in the organometallic chemistry of the transition metals and the lanthanide metals.⁴

Previously, most syntheses of stable organolanthanides involving lanthanide-carbon σ bonds have used the cyclopentadienyl ligand as a bulky stabilizing ligand,^{2b} although homoleptic 2,6-dimethylphenyl complexes have been known⁵ since 1972 and demonstrate that the cyclopentadienyl ligand is not essential. Recently, the silyl ligands $-\text{CH}_2\text{Si}(\text{CH}_3)_3$ and $-\text{CH}[\text{Si}(\text{CH}_3)_3]_2$, commonly used in organo transition metal synthesis because they lack β hydrogens,⁶ have been used to form stable organolanthanides.⁷ The results described below demonstrate that it is unnecessary to limit syntheses of σ -bonded organolanthanides to ligands which lack β hydrogens.

Slow addition of a freshly prepared pentane solution of $t\text{-C}_4\text{H}_9\text{Li}$ ⁸ to a magnetically stirred suspension of anhydrous LnCl_3 ⁹ ($\text{Ln} = \text{Sm}, \text{Er}, \text{Yb}$)¹⁰ in THF at -55°C , followed by stirring for 1 hour, warming to room temperature, and stirring for an additional 2 h, affords a solution which has the distinctive color of the trivalent lanthanide ion and a fine precipitate of LiCl . Filtration and solvent removal yields an oily mass which is washed with pentane to remove traces of alkyllithium and extracted with diethyl ether to separate any remaining LiCl . THF is added to the ether solution, all solvent is removed, and the process repeated until free-flowing powders are obtained (yield 50–75%). Further purification may be effected via crystallization of these compounds induced by slow diffusion of pentane into a concentrated THF-hexane solution.

All of the complexes are extremely air and moisture sensitive. The erbium derivative appears less sensitive than the ytterbium and samarium compounds, which decompose to white powders within seconds of air exposure. The erbium complex is also the most thermally stable complex in the series and begins to decompose at 60°C in vacuo.¹¹ The samarium and ytterbium compounds appear to decompose slowly at room temperature over a period of several days. The compounds are insoluble in hydrocarbon solvents and are converted to oils by aromatic solvents. They are completely soluble in diethyl ether and THF.

The composition of the *tert*-butyl complexes has been verified by an accurate and complete elemental analysis of the most stable erbium complex¹² and by complexometric metal analyses of the other members of the series.¹³ As expected, hydrolysis of the complexes yields THF and 2-methylpropane.¹⁴

The infrared spectra of the complexes¹⁵ are virtually identical exhibiting sharp absorptions at 1045 and 890 cm^{-1} characteristic of coordinated THF¹⁶ and absorptions at 1455, 1180, 1135, and 780 cm^{-1} which may be assigned to the *tert*-butyl group. Absorptions at 2760, 2730, 2670, and 2620 cm^{-1} are attributable to $\text{Li-H}_3\text{C}$ interactions¹⁷ suggesting that the lithium cation is not completely surrounded by solvating THF molecules. Each complex exhibits a near-IR-visible spectrum characteristic of the free trivalent ion.¹⁸ The erbium spectrum is particularly interesting in that the absorptions at 526 and 383 nm due to transitions from the $^4I_{15/2}$ ground manifold to $^2H_{11/2}$ and $^4G_{11/2}$, respectively, are hypersensitive.¹⁹

Variable-temperature magnetic susceptibility measurements²¹ confirm the +3 oxidation state of the metal in these complexes (Table I). As expected, the erbium and ytterbium compounds obey the Curie-Weiss law, while the samarium complex does not. Only for the samarium derivative was a ^1H

Table I

compd	color	$10^6 \chi_M$, cgs (corr)	μ_{eff} (280 K)	θ (K)
$\text{LiEr}(t\text{-C}_4\text{H}_9)_4(\text{THF})_4$	pink	43200	9.7	10
$\text{LiYb}(t\text{-C}_4\text{H}_9)_4(\text{THF})_3$	red-purple	9500	4.6	2
$\text{LiSm}(t\text{-C}_4\text{H}_9)_4(\text{THF})_4$	dark gold	2000	2.1	

NMR spectrum observable in the normal region and the sharp singlet at $\delta -0.79$ was assigned to the 36 equivalent protons contained in the 4 equivalent *tert*-butyl groups.

Thermal decomposition of the samarium derivative could be conveniently monitored via NMR and showed a decrease in the $\delta -0.79$ singlet with concomitant appearance of absorptions for 2-methylpropane²⁴ during a 12-h period in THF at 40°C . The decomposition was complete after 16 h, and quantitative measurements indicated that 3.25 mol of 2-methylpropane had formed/mol of $\text{LiSm}(t\text{-C}_4\text{H}_9)_4(\text{THF})_4$. The only other major organic product observed was 0.5 mol of ethylene, presumably formed by attack of free $t\text{-C}_4\text{H}_9\text{Li}$ on THF.²⁵ Since the infrared spectra indicate that Li is already interacting to some extent with the *tert*-butyl groups, it is reasonable to suggest that dissociation of $t\text{-C}_4\text{H}_9\text{Li}$ occurs as one of the initial decomposition steps. Consistent with this proposal is the decomposition of $\text{LiSm}(t\text{-C}_4\text{H}_9)_4(\text{C}_4\text{D}_8\text{O})_4$ ²⁶ in $\text{C}_4\text{D}_8\text{O}$. The 2-methylpropane formed is $\sim 25\%$ $(\text{CH}_3)_3\text{CD}$ suggesting that only one of the four *tert*-butyl groups reacts with THF to form 2-methylpropane.^{27,28}

The absence of equivalent quantities of 2-methylpropene and 2-methylpropane in this decomposition is remarkable and suggests that β -hydride elimination is not the most facile decomposition pathway. This result contrasts sharply with organo transition metal chemistry, where the ease of β -hydride elimination usually precludes the formation of stable *tert*-butyl species.²⁹ The only reported homoleptic *tert*-butyl transition metal complex, $\text{Cr}(t\text{-C}_4\text{H}_9)_4$,³ presumably is stable owing to an interlocking cogwheel arrangement of ligands which prevents close approach of the β hydrogen and the metal. Nonetheless, β -hydride elimination is one of the reaction pathways in the thermal decomposition of $\text{Cr}(t\text{-C}_4\text{H}_9)_4$ which occurs in 1 h at 70°C to form 2-methylpropene, 2-methylpropane, methane, ethane, and propane.³ Since the lanthanide metal center is substantially larger than that of chromium,³⁰ geometrical restraints to β -hydride elimination are unlikely unless the solvating THF molecules significantly affect chemical reactivity at the metal center by occupying vacant coordination sites.²⁸ The origins and practical utility of these unusual reactivity patterns observed for these organolanthanides are under investigation.

Acknowledgment. Support of this research by the Division of Basic Energy Sciences of the Department of Energy is gratefully acknowledged. We also thank Bell Laboratories for a fellowship (to A.L.W.) under the Bell Laboratories Graduate Research Program for Women and Dr. J. W. Mitchell and Mr. L. D. Blitzer for helpful discussion.

References and Notes

- (1) Presented in part at the 176th National Meeting of the American Chemical Society, Miami Beach, Fla., Sept 11, 1978.
- (2) (a) E. C. Baker, G. W. Halstead, and K. N. Raymond, *Struct. Bonding (Berlin)*, **25**, 23 (1976); (b) M. Tsutsui, N. Ely, and R. Dubois, *Acc. Chem. Res.*, **9**, 217 (1976); (c) B. Kanellakopoulos and K. W. Bagnall, *MTP Int. Rev. Sci.*, **7**, Chapter 8 (1972); (d) R. G. Hayes and J. L. Thomas, *Organomet. Chem. Rev. A*, **7**, 1 (1971).
- (3) W. Kruse, *J. Organomet. Chem.*, **42**, C39 (1972).
- (4) W. J. Evans, S. C. Engerer, and A. C. Neville, *J. Am. Chem. Soc.*, **100**, 331 (1978); (b) W. J. Evans, A. L. Wayda, C. W. Chang, and W. M. Cwirla, *ibid.*, **100**, 333 (1978).
- (5) S. A. Cotton, F. A. Hart, M. B. Hursthouse, and A. J. Welch, *J. Chem. Soc. Chem. Commun.*, 1225 (1972).
- (6) (a) G. Wilkinson, *Pure Appl. Chem.*, **30**, 627 (1972); (b) C. S. Cundy, B. M.

- Kingston, and M. F. Lappert, *Adv. Organomet. Chem.*, **11**, 253 (1973).
- (7) (a) H. Schumann and J. Müller, *J. Organomet. Chem.*, **146**, C5 (1978). (b) J. L. Atwood, W. E. Hunter, R. D. Rogers, J. Holton, J. McMeeking, R. Pearce, M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 140 (1978). (c) Phenylethynyl complexes are also known: G. B. Deacon and A. J. Koplick, *J. Organomet. Chem.*, **146**, C43 (1978).
- (8) Commercially prepared $t\text{-C}_4\text{H}_9\text{Li}$ (Aldrich) may be used, but purer compounds are obtained by use of freshly prepared (adapted from L. J. Tyler, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2876 (1948)) and titrated (C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967)) reagent. Typically, $t\text{-C}_4\text{H}_9\text{Li}$ (25 mM in 30 mL of pentane) is added over 15–30 min to a slurry of LnCl_3 (6 mM) in 30 mL of THF. All reactions were conducted in an inert atmosphere using standard techniques (D. F. Shriver, "Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, 1969).
- (9) M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, **24**, 387 (1962).
- (10) The lighter lanthanides do not give similar complexes. For example, with $\text{Ln} = \text{Pr}$, a compound is isolated which differs markedly from the title complexes. The identity and properties of this compound and related light lanthanide analogues are under investigation.
- (11) Decomposition is accompanied by a distinctive color change to dark orange. The decomposition product is insoluble in all common organic solvents and exhibits a featureless IR spectrum.
- (12) Anal. Calcd for $\text{LiErC}_{32}\text{H}_{68}\text{O}_4$: Er, 24.20; Li, 1.00; C, 55.62; H, 9.92; O, 9.26. Found: Er, 24.42; Li, 1.12; C, 55.35; H, 9.70; O, 9.41 (by difference) (Bernhardt).
- (13) Anal. Calcd for $\text{LiYbC}_{28}\text{H}_{60}\text{O}_3$: Yb, 27.70. Found: Yb, 26.8. Calcd. for $\text{LiSmC}_{32}\text{H}_{68}\text{O}_4$: Sm, 22.30. Found: Sm, 23.4. (Determined by hydrolysis of a weighed sample followed by direct titration with 0.01 M $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ with xylenol orange as indicator.) The instability of the samarium and ytterbium compounds precludes normal commercial analyses. However, data from Bernhardt on the complexes is supportive though not complete.
- (14) Hydrolysis is accomplished by addition of excess H_2O to a sample of the complex under a layer of deuteriobenzene. The organic products extracted into the deuteriobenzene were identified by NMR.
- (15) $\text{LiEr}(t\text{-C}_4\text{H}_9)_4(\text{THF})_4$: IR (Nujol, cm^{-1}) 2730 (s), 2670 (s), 2620 (m), 1455 (s, discernible from Nujol), 1297 (w), 1250 (w, br), 1180 (w, br), 1135 (s), 1045 (s), 990 (m), 940 (m), 920 (m), 890 (s), 780 (s), 730 (w), 720 (sh, w), 675 (w).
- (16) R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, 379 (1963).
- (17) R. A. Andersen, E. Carmona-Guzman, J. F. Gibson, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 2204 (1976).
- (18) Near-IR-visible (in THF) (λ_{max} , nm (ϵ)): $\text{LiEr}(\text{C}_4\text{H}_9)_4(\text{THF})_4$, 997, 979, 668, 656, 536 (40), 532 (sh), 529 (65), 526 (120), 490, 451, 444, 406, 388 (75), 385 (sh), 383 (260); $\text{LiSm}(\text{C}_4\text{H}_9)_4(\text{THF})_4$, 1551 (sh), 1499, 1392, 1271 (sh), 1242 (9), 1091 (9), 955; $\text{LiYb}(\text{C}_4\text{H}_9)_4(\text{THF})_3$, 993 (35), 949 (sh), 500 (shoulder on charge-transfer band).
- (19) (a) R. D. Peacock, *Struct. Bonding (Berlin)*, **22**, 83 (1975). (b) R. Pappalardo, *J. Chem. Phys.*, **49**, 1545 (1968). (c) N. M. Ely and M. Tsutsui, *Inorg. Chem.*, **14**, 2680 (1975). (d) Analysis of the $^4I_{15/2} \rightarrow ^2H_{1/2}$ transition by Karkar's arguments correlating hypersensitive band shape with coordination number²⁰ would suggest that the Er^{3+} ion is eight coordinate in the complex, implying that the Er^{3+} coordination environment consists of four *tert*-butyl groups and four THF ligands with the unsolvated lithium cation interacting only with the methyl groups of the *tert*-butyl ligands. Although this is consistent with the infrared evidence, this argument suggests an unreasonably crowded coordination sphere for Er^{3+} . A crystallographic investigation will be required to determine if Karkar's arguments for oxygen donor atom ligands can be extended to alkyl ligands.
- (20) D. G. Karkar, *Inorg. Chem.*, **6**, 1863 (1967).
- (21) Susceptibilities were measured using the Evans' method²² with the modified equation,²³ $\chi = 3\Delta f/4\pi fm + \chi_0$, appropriate for a Bruker 270-MHz NMR spectrometer. A Faraday measurement on the erbium sample of 9.37 μB was consistent with the solution measurement.
- (22) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
- (23) J. K. Becconsall, *Mol. Phys.*, **15**, 129 (1968).
- (24) Subsequently identified by GC-mass spectrometry.
- (25) J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69**, 693 (1969).
- (26) Formed by exchanging $\text{LiSm}(t\text{-C}_4\text{H}_9)_4(\text{C}_4\text{H}_8\text{O})_4$ with $\text{C}_4\text{H}_8\text{O}$ until $\text{C}_4\text{H}_8\text{O}$ incorporation was <1%. The completeness of the exchange was confirmed by decomposition in CDCl_3 .
- (27) After decomposition, a brown soluble samarium complex remains. Since this product exhibits no NMR signals in the diamagnetic region, it is presumably not a complex of the alkoxides formed from the decomposition of THF.
- (28) In contrast, the oil which forms when $\text{LiSm}(t\text{-C}_4\text{H}_9)_4(\text{THF})_4$ is placed in benzene decomposes by a different route. 2-Methylpropane is still the primary product, but the decomposition is incomplete and some 2-methylpropene is observed. The effect of solvent on these decompositions and the identity of the samarium products remaining after decomposition are currently under investigation.
- (29) P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, **76**, 219 (1976).
- (30) For example, in oxides Er^{3+} has an effective ionic radius of 0.88 Å compared with 0.44 Å for four-coordinate Cr^{4+} .³¹
- (31) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

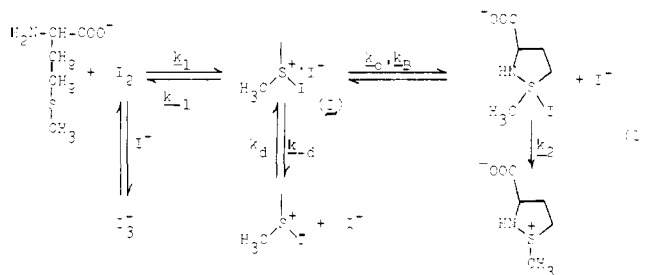
Andrea L. Wayda, William J. Evans*

Department of Chemistry, University of Chicago
Chicago, Illinois 60637
Received May 30, 1978

General Base Catalysis and Evidence for a Sulfurane Intermediate in the Iodine Oxidation of Methionine

Sir:

The oxidation of methionine by iodine to give the cyclic sulfimine dehydromethionine (*S*-methylisothiazolidine-3-carboxylic acid) is catalyzed by general bases and gives a nonlinear Brønsted plot which breaks from a slope of ~ 1.0 to a slope of zero at approximately $\text{p}K_a = 2$. This is interpreted as evidence for a mechanism involving stepwise proton transfer through a preassociation mechanism. At low concentration of buffer, the reaction is inversely dependent on the concentration of iodide ion. At high buffer concentration, the reaction rates exhibit a nonlinear dependence on iodide concentration which approaches an inverse-squared dependence. The observation of a simple inverse dependence at low buffer requires that diffusion apart of the iodosulfonium ion-iodide encounter complex (1) must be slow with respect to reduction of the complex through k_{-1} and ring closure through k_0 (eq 1). The



changeover to an inverse-squared dependence at high buffer requires a kinetically significant intermediate *after* the ring closure step. It is suggested that this intermediate is a tetra-coordinate sulfurane.

The iodine oxidation of sulfides proceeds through the initial formation of an iodosulfonium ion.¹ Typically, this intermediate can be attacked by iodide ion, reversing the reaction, or by water to give the sulfoxide. A major unanswered question in nucleophilic reactions of these types is whether the attack occurs through an $\text{S}_\text{N}2$ -like transition state or if a tetra-coordinate sulfurane is involved as an obligatory intermediate.² In the iodine oxidation of methionine, the proximal amino group apparently traps the iodosulfonium ion intermediate faster than that intermediate is attacked by the solvent to give sulfoxide. In its simplest form, this mechanism predicts an inverse-squared dependence on the concentration of iodide ion: one inverse dependence as a result of the equilibrium to give triiodide ion and the second due to reversal of the oxidation process by attack of iodide on the iodosulfonium ion. The observation by us and others³ that this reaction shows a simple inverse dependence at low buffer concentrations requires that either attack be rate limiting or that free iodide in solution does not reduce the iodosulfonium ion intermediate. Since buffer catalysis is observed, it is unlikely that attack of iodine is rate limiting. Therefore, the rate constants for reversion of the iodosulfonium ion-iodide encounter pair back to starting materials (k_{-1}) and the rate constant for ring closure (k_0) must be faster than the rate constant for diffusion apart of the ion pair. Since the ion pair is not expected to be extraordinarily stable, this suggests that k_{-1} and k_0 will also be faster than the rate constant for diffusion of 1 M buffer base up to the encounter pair. This requires that the buffer preassociate with the methionine-iodine complex *before* the oxidation step occurs and that the catalysis occur through either a concerted or a stepwise-preassociation mechanism.⁴ While those two mechanisms can theoretically be distinguished based on their Brønsted behavior, the data do not rigorously exclude a linear