= 14.4 Hz, $^3J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 3.3 Hz, and $^3J_{HH}$ = 3.0 Hz), 1.67 (dtt, 1 H, $^2J_{HH}$ = 16.2 Hz, $^3J_{HH}$ = 7.7 Hz, and $^3J_{HH}$ = 1.1 Hz), 1.33 (dtt, 1 H, $^2J_{HH}$ = 16.2 Hz, $^3J_{HH}$ = 10.6 Hz, $^3J_{HH}$ < 0.5 Hz), 0.25 (ddddd, 2 H, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 12.3 Hz, $^3J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 3.3 Hz, and $^3J_{HH}$ = 1.1 Hz). ^{1}H NMR data are in agreement with published data.[15] ^{2}H NMR (38.39 MHz, diethyl ether/diethyl ether-d_{10} 1:1) δ 7.90 (s), 7.21 (t, $^3J_{HD}$ = 0.9 Hz); mass spectrum m/z (%, fragment) 148 (38, $M^{+\cdot}$), 133, (43, $[M - CH_3]^+$), and 106 (100). On the basis of the ^{1}H NMR spectrum of **1d** the deuterium incorporation at C-8 was 97% and at C-11 it was 81%.

1,3-Diethyl[2-^{2}H]benzene (3e) or 1,3-Diisopropyl[2-^{2}H]benzene (4e). To a solution of 1,3-diethyl- or 1,3-diisopropyl-2-bromobenzene (47 mmol) in dry diethyl ether (7 mL), *n*-butyllithium in *n*-hexane (10 mmol) was added. After being heated at reflux temperature for 5 h, the reaction mixture was cooled to room temperature and D_2O (1 mL) was added. The organic layer was separated, washed with water (5 mL) and brine (5 mL), dried ($MgSO_4$), and concentrated at reduced pressure. The crude product was purified by preparative GLC (15% SE-30, Chromosorb W-60M, 1.5 m, 100 °C) to yield **3e** and **4e**, respectively, as a colorless liquid. **3e** (0.61 g, 4.5 mmol 95%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.31-6.93 (AB_2 system δ_A 7.22, δ_B 7.02, 3 H, J_{AB} = 8.0 Hz), 2.65 (q, 4 H, $^3J_{HH}$ = 7.6 Hz), and 1.25 (t, 6 H, $^3J_{HH}$ = 7.6 Hz); ^{2}H NMR (38.39 MHz, diethyl ether/diethyl ether-d_{10} 1:1) δ 7.08 (s); mass spectrum m/z (%, fragment) 135 (43, $M^{+\cdot}$), 120 (85, $[M - CH_3]^+$) and 106 (100, $[M - C_2H_5]^+$). On the basis of the ^{1}H NMR spectrum the deuterium incorporation at C-2 was 80%. **4e** (0.69 g, 4.23 mmol, 90%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.42-6.96 (AB_2 system δ_A 7.29, δ_B 7.11, 3 H, J_{AB} = 8.0 HZ), 2.86 (2 H, M), 1.22 (D, 12 H, $^3J_{HH}$ = 6.9 HZ); ^{2}H NMR (38.39 MHz, diethyl ether/diethyl ether-d_{10} 1:1) δ 7.14 (s); mass spectrum m/z (%, fragment) 163 (38, $M^{+\cdot}$) and 148 (100, $[M - CH_3]^+$). On the basis of the ^{1}H NMR spectrum the deuterium incorporation at C-2 was 80%.

1,3-Dimethyl[2,5-$^2H_2$]benzene (2d). Compound **2d** was prepared from 2,5-dibromo-1,3-dimethylbenzene (**2c**) by a procedure similar to that described for **3e** and **4e**. Direct dilithiation was impossible under our reaction conditions, probably as a consequence of the low solubility of the monolithiated compound. Therefore, the monolithiated compound was quenched with D_2O and after workup subjected to another reaction sequence as described above. The intermediate product was identified to be 2-bromo-1,3-dimethyl[5-^{2}H]benzene (**2f**). Compound **2f** is a colorless liquid (0.63 g, 3.4 mmol, 90%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.07 (2 H, br s), 2.42 (6 H, s); ^{2}H NMR (38.39 MHz, diethyl ether/diethyl ether-d_{10} 1:1) δ 7.15 (t, $^3J_{HD}$ = 1.0 Hz); mass spectrum m/z (%, fragment) 185 (52, $M^{+\cdot}$) and 106 (100, $[M - Br]^+$). On the basis of the ^{1}H NMR spectrum the deuterium incorporation at C-5 was 95%. Compound **2d** is a colorless liquid (0.25 g, 2.3 mmol, 68%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.99 (2 H, s), 2.33 (6 H, s); ^{2}H NMR (diethyl ether/diethyl ether-d_{10} 1:1) δ 7.15 (t, $^3J_{HD}$ = 1.2 Hz), 7.03 (s); mass spectrum m/z (%, fragment) 108 (70, $M^{+\cdot}$) and 93 (100, $[M - CH_3]^+$). On the basis on the ^{1}H NMR spectrum the deuterium incorporation at C-2 was 70%.

Acknowledgment. The authors thank P. A. Kraakman, Dr. F. J. J. de Kanter, and C. Skoglund for experimental help and Professors Bothner-By and Dadok are acknowledged for discussions and for access to the 14.1-T NMR Facility for Biomedical studies in Pittsburgh, The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). P.C.M.v.Z. and C.M. are grateful for a NATO travel grant (RG 486.82) which strongly facilitated this research.

Registry No. **1c**, 96426-52-7; **1d**, 100243-46-7; **2c**, 100189-84-2; **2d**, 100189-86-4; **2f**, 100189-85-3; **3e**, 100189-82-0; **4e**, 100189-83-1; 1,3-diethyl-2-bromobenzene, 65232-57-7; 1,3-diisopropyl-2-bromobenzene, 57190-17-7.

Efficient Detection and Evaluation of Cyclodextrin Multiple Complex Formation

Daniel W. Armstrong,* Faruk Nome, Larry A. Spino, and Teresa D. Golden

Contribution from the Department of Chemistry, Texas Tech University, Lubbock, Texas 79409.
Received July 3, 1985

Abstract: Equations are derived which allow one to determine α-cyclodextrin–substrate complex stoichiometries as well as primary and secondary binding constants by using liquid chromatographic retention values. Retention is dependent on the concentration of cyclodextrin in the mobile phase as well as the stoichiometry of the cyclodextrin–substrate complex. It was found that two cyclodextrin molecules bind to prostaglandin B_1, prostagladin B_2, 4,4′-biphenol, and *p*-nitroaniline. Conversely, *o*-nitroaniline and *m*-nitroaniline form complexes of 1:1 stoichiometry. The fact that closely related compounds such as the nitroanilines can exhibit different binding behaviors may result in the reevaluation of some cyclodextrin-based studies.

The ability of cyclodextrins (CDs) and synthetically modified cyclodextrins to form inclusion complexes with a variety of molecules is well-known.[1-6] Cyclodextrins have been used as enzyme models,[1,2,6-8] catalysts,[9,10] emulsifiers,[11] novel reaction media,[12] stationary phases for chiral and isomeric separations,[13-16] and so on. Because of their unique properties and inherent usefulness, several basic studies have been done to evaluate cyclodextrin complexation. Most of these studies assume a 1:1 stoichiometry between the cyclodextrin host and the guest molecule of interest. However, a few research groups have reported that in some cases, two or more cyclodextrins can bind to a single solute.[17-24] Indeed this phenomenon may be a good deal more

(1) Griffiths, D. W.; Bender, M. L. "Advances in Catalysis"; Eley, D. D., Pines, H., Weisz, P. B., Eds.; Academic: New York, 1973; Vol. 23, p 209.
(2) Bender, M. L.; Komiyama, M. "Cyclodextrin Chemistry"; Springer-Verlag: Berlin, 1978.
(3) Hinze, W. L. *Sep. Purif. Methods* **1981**, *10*, 159.
(4) Szejtli, J. "Cyclodextrins and Their Inclusion Complexes"; Akademai Kiado: Budapest, 1982.
(5) Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66.
(6) Breslow, R. *Science* **1982**, *218*, 532.
(7) Van Etten, R. L.; Sebastian, J. F.; Clowes, G. A.; Bender, M. L. *J. Am. Chem. Soc.* **1967**, *89*, 3242-3253, 3253-3262.
(8) Siegel, B.; Breslow, R. *J. Am. Chem. Soc.* **1975**, *97*, 6869.
(9) Trainor, G. L.; Breslow, R. *J. Am. Chem. Soc.* **1981**, *103*, 154.
(10) Breslow, R.; Trainor, G.; Veno, A. *J. Am. Chem. Soc.* **1983**, *105*, 2739.
(11) Menger, F. M.; Dulany, M. A. *Tetrahedron Lett.* **1985**, *26*, 267.
(12) le Noble, W. J.; Srivastava, S.; Breslow, R.; Trainor, G. *J. Am. Chem. Soc.* **1983**, *105*, 2745.
(13) Armstrong, D. W.; DeMond, W. *J. Chromatogr. Sci.* **1984**, *22*, 411.
(14) Armstrong, D. W.; DeMond, W.; Alak, A.; Hinze, W. L.; Ried, T. E.; Bui, K. H. *Anal. Chem.* **1985**, *57*, 234.
(15) Hinze, W. L.; Riehl, T. E.; Armstrong, D. W.; DeMond, W.; Alak, A.; Ward, T. *Anal. Chem.* **1985**, *57*, 237.
(16) Armstrong, D. W.; DeMond, W.; Czech, B. P. *Anal. Chem.* **1985**, *57*, 481.
(17) Harata, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1493.

0002-7863/86/1508-1418$01.50/0

common than previously believed. It is apparent that the interpretation of kinetic, synthetic, and chiral interaction data could be significantly altered if multiple cyclodextrin complexes are formed.

Laufer and co-workers were able to determine the ratio of binding constants of 1:2 (substrate:CD) complexes using conductometric titrations.[18] However, values for individual constants could not be obtained. Connors and co-workers utilized potentiometric and spectrophotometric methods to determine the binding constants of two cyclodextrins to several substituted anilines.[22] Unfortunately, either the second binding constant was unobtainable or the relative error for the second constant was substantial. Connors and co-workers subsequently evaluated techniques which utilized solubility and competitive indicator binding.[23,24] It was reported that one could obtain both primary and secondary binding constants using these methods. It should be noted that there are also cases where two guest molecules bind to a single cyclodextrin host.[4] These particular ternary complexes will not be considered in this report, however.

In this work it is demonstrated that liquid chromatography with cyclodextrin mobile phases can be used to evaluate the stoichiometry and all relevant binding constants for most CD–substrate systems, This method is not dependent on a solute's spectroscopic properties, conductivity, electrochemical behavior, or solubility. Cyclodextrin mobile phases previously have been used to evaluate single binding constants;[25-27] however, neither the theory nor chromatographic experimental evidence of cyclodextrin multiple complex formation has been reported to our knowledge.

Experimental Section

Materials. Bulk α-cyclodextrin and 10 cm γ-cyclodextrin bonded phase columns (Cyclobond II) were obtained from Advanced Separation Technologies, Inc. Polygram polyamide-6 UV_{254} thin-layer chromatographic sheets were obtained from Brinkmann. HPLC-grade water was obtained from Burdick & Jackson. The α-cyclodextrin was purified by precipitation from HPLC-grade water with Aldrich 99+% gold label 1,1,2-trichloroethylene. The precipitate was isolated, washed, and resuspended in HPLC-grade water. The suspension was boiled to steam distill the trichloroethylene. When the trichloroethylene was removed a homogeneous solution of α-CD remained. The solution was lyophilized to recover pure α-CD.

Methods. All isocratic LC separations were done at room temperature (21 °C) with a Shimadzu Model LC-4A liquid chromatograph with a variable wavelength detector. The prostagladins were detected at 280 nm and all aromatic compounds were detected at 254 nm. Note that any detector can be used provided it is compatible with the compound of interest. All TLC developments were done in a Chromaflex developing tank. Seven standard α-CD mobile phase solutions were used (between 0.01 and 0.1 M). TLC spots were visualized either by fluorescence quenching or by using a dilute $KMnO_4$ spray reagent.

Results and Discussion

It is well-known that one can use LC and various forms of the pseudophase retention equation to determine the binding constant or partition coefficient of a solute to a cyclodextrin molecule or a micelle.[25,28] One of the simplifying assumptions made for all of these treatments is that the stoichiometry is 1:1. In cases where two or more cyclodextrins bind to a solute, traditional equations give curves of increasing slope rather than the straight lines predicted by theory. However, appropriate expressions which take into account multiple CD complexation are easily formulated. For a 1:2 (substrate:cyclodextrin) complex the following four equilibria must be considered:

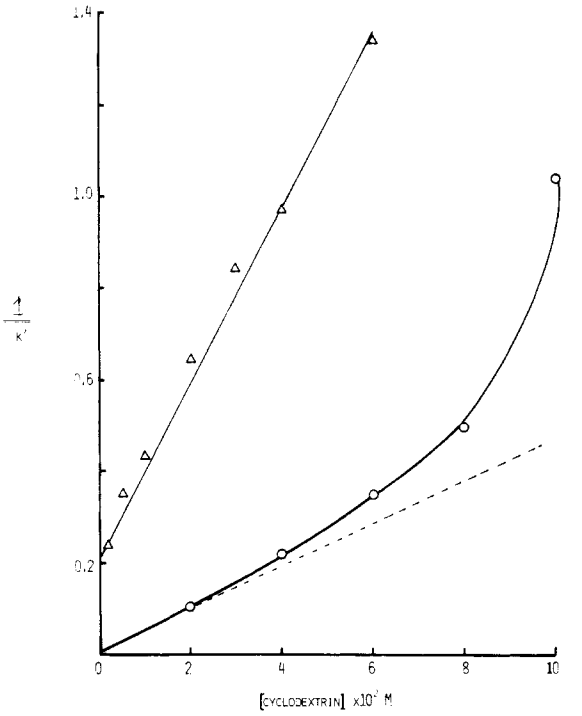

Figure 1. Plots of $1/k'$ vs. α-CD concentration illustrating the different retention behavior of 1:1 complexes (Δ,m-nitroaniline) and 2:1 complexes (O, prostaglandin B_1). The dashed line is the limiting slope.

$$S + A \overset{K}{\rightleftharpoons} SA \qquad K = \frac{[SA]}{[S][A]} \tag{1}$$

$$S + CD \overset{K_1}{\rightleftharpoons} SCD \qquad K_1 = \frac{[SCD]}{[S][CD]} \tag{2}$$

$$SCD + CD \overset{K_2}{\rightleftharpoons} S(CD)_2 \qquad K_2 = \frac{[S(CD)_2]}{[SCD][CD]} \tag{3}$$

$$S + 2CD \overset{K_1K_2}{\rightleftharpoons} S(CD)_2 \qquad K_1K_2 = \frac{[S(CD)_2]}{[S][CD]^2} \tag{4}$$

where S is the free solute being chromatographed, A is a stationary phase adsorption site, CD is a cyclodextrin molecule, SCD is a 1:1 solute:cyclodextrin complex, $S(CD)_2$ is a 1:2 solute:cyclodextrin complex, and the respective equilibrium constants are K, K_1, and K_2. Consequently the total amount of solute (S_{tot}) is given by

$$S_{tot} = S + SA + SCD + S(CD)_2 \tag{5}$$

Using the standard chromatographic definition of capacity factor (k') for this system one obtains

$$k' \text{ or } \frac{1 - R_f}{R_f} = \frac{\Phi[SA]}{[S] + [SCD] + [S(CD)_2]} \tag{6}$$

where Φ is the phase ratio and R_f is the retardation factor of a solute in thin-layer chromatography. Replacing [SA], [SCD], and $[S(CD)_2]$ using equations 1–4 one obtains

$$k' = \frac{\Phi K[A][S]}{(1 + K_1[CD] + K_1K_2[CD]^2)[S]} \tag{7}$$

Cancelling [S] and rearranging this expression gives an equation which describes the LC retention behavior of solutes which complex two cyclodextrin molecules.

$$\frac{1}{k'} \text{ or } \frac{R_f}{1 - R_f} = \frac{1}{\Phi K[A]} + \frac{K_1[CD]}{\Phi K[A]} + \frac{K_1K_2[CD]^2}{\Phi K[A]} \tag{8}$$

(18) Gelb, R. I.; Schwartz, L. M.; Murray, C. T.; Laufer, D. A. *J. Am. Chem. Soc.* **1978**, *100*, 3553.
(19) Gelb, R. I.; Schwartz, L. M.; Laufer, D. A. *J. Am. Chem. Soc.* **1978**, *100*, 5875.
(20) Gelb, R. I.; Schwartz, L. M.; Johnson, R. F.; Laufer, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1869.
(21) Connors, K. A.; Rosanske, T. W. *J. Pharm. Sci.* **1980**, *69*, 173.
(22) Wong, A. B.; Lin, S.-F.; Connors, K. A. *J. Pharm. Sci.* **1983**, *72*, 388.
(23) Connors, K. A.; Pendergast, D. D. *J. Am. Chem. Soc.* **1984**, *106*, 7607.
(24) Pendergast, D. D.; Connors, K. A. *J. Pharm. Sci.* **1984**, *73*, 1779.
(25) Armstrong, D. W.; Stine, G. Y. *J. Am. Chem. Soc.* **1983**, *105*, 2962.
(26) Sybilska, D.; Lipkowski, J.; Wöycikowski, J. *J. Chromatogr.* **1982**, *253*, 95.
(27) Sybilska, D.; Debowski, J.; Jurczak, J.; Zukowski, J. *J. Chromatogr.* **1984**, *286*, 163.

Table I. Variation in the Capacity Factors (k') of a Series of Compounds with Increasing Concentration of α-Cyclodextrin in the Mobile Phase

	concn of α-cyclodextrin, M						
compound	0.1	0.08	0.06	0.04	0.03	0.02	0.01
prostaglandin B_1	1.41	2.03	2.85	4.60		10.20	
prostaglandin B_2	3.45	4.60	6.67	10.40		21.74	
4,4′-biphenol			0.14	0.34	0.51	1.11	2.93
o-nitroaniline			3.90	5.00	5.45	6.22	7.65
m-nitroaniline			0.72	1.03	1.18	1.55	2.31
p-nitroaniline			0.04		0.12	0.24	0.58

If $K_2 = 0$, this equation reduces to the usual equation for linear behavior.[25,28] This same approach can be used to derive expressions for higher complexes. Furthermore, one can easily modify these equations to take into account the ionization of weak acids and bases as was done by Sybilska et al.[26,27] for solutes of 1:1 stoichiometry.

Plots of $1/k'$ or $R_f/(1 - R_f)$ vs. cyclodextrin concentration (eq 8) give curves in which the *limiting slope* corresponds to $K_1/(\Phi K[A])$ and the intercept is $1/(\Phi K[A])$ (see Figure 1). From the ratio of slope over intercept one can calculate K_1. Plots of $1/k'$ or $R_f/(1 - R_f)$ vs. $[CD]^2$ give a linear region at moderate to high cyclodextrin concentrations. The slope of this line is equal to $K_1K_2/(\Phi K[A])$. This allows one to obtain the product K_1K_2.

One problem with the above technique is that the intercept of the first plot is frequently near zero and therefore $1/\Phi K[A]$ is inaccurate or unknown. Furthermore, a direct determination of K_2 would be desirable. Consequently an alternative method is proposed. When the intercept of eq 8 approaches zero this expression can be simplified to

$$\frac{1}{k'} \text{ or } \frac{R_f}{1 - R_f} = \frac{K_1[CD]}{\Phi K[A]} + \frac{K_1K_2[CD]^2}{\Phi K[A]} \quad (9)$$

and rearranged to

$$\frac{1}{k'[CD]} \text{ or } \frac{R_f}{(1 - R_f)[CD]} = \frac{K_1}{\Phi K[A]} + \frac{K_1K_2[CD]}{\Phi K[A]} \quad (10)$$

According to eq 10 a plot of $1/(k'[CD])$ vs. cyclodextrin concentration should be linear and have a slope of $K_1K_2/(\Phi K[A])$ and intercept of $K_1/(\Phi K[A])$ for cyclodextrin complexes of 2:1 stoichiometry. The ratio of slope over intercept provides a direct value for K_2.

Table I gives the retention data for several compounds as a function of cyclodextrin concentration in the mobile phase. Representative plots of eq 8 are given in Figure 1. When the cyclodextrin–solute stoichiometry is one to one ($K_2 = 0$) straight-line plots are obtained as for *m*-nitroaniline in the upper curve of Figure 1. *o*- and *m*-nitroaniline exhibit this type of behavior. The lower curve of Figure 1 is indicative of the behavior of solutes which bind more than one cyclodextrin (e.g., prostaglandin B_1, prostaglandin B_2, 4,4′-biphenol, and *p*-nitroaniline). One would expect linear plots of $1/k'$ vs. the square of cyclodextrin concentration for solutes which bind two cyclodextrin molecules. This is illustrated in Figure 2. At low cyclodextrin concentrations these plots are expected to curve toward zero. A direct determination of the second binding constant (K_2) can be accomplished by plotting eq 10 as illustrated in Figure 3. When doing these plots one should avoid using retention volumes near the dead volume of the column (which produce erroneous results).

Table II gives the stoichiometry, calculated binding constants, and standard deviations of five compounds with α-cyclodextrin with use of the aforementioned techniques (eq 8 and 10). It is interesting to note that *p*-nitroaniline appears to be able to bind two cyclodextrin molecules while the ortho and meta isomers bind only one. One can speculate on the type of interactions that result in the formation of multiple complexes. In the case of 4,4′-biphenol, one can envision two α-CD molecules complexing at opposite ends of a symmetrical molecule. However, it is unlikely that this could occur with *p*-nitroaniline, particularly when considering its size and the disparity in K_1 and K_2. It is more likely that one cyclodextrin forms an inclusion complex while the second

(28) Armstrong, D. W. *Sep. Purif. Methods* **1985**, *14*, 213.

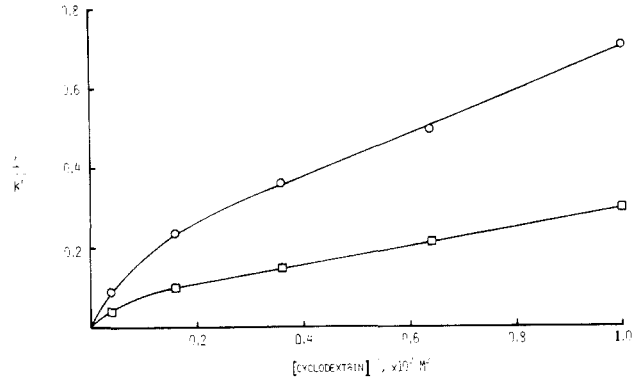

Figure 2. Plots of $1/k'$ vs. the square of α-CD concentration are linear for 2:1 complexes such as prostaglandin B_1 (○) and prostaglandin B_2 (□) except at very low concentrations of CD.

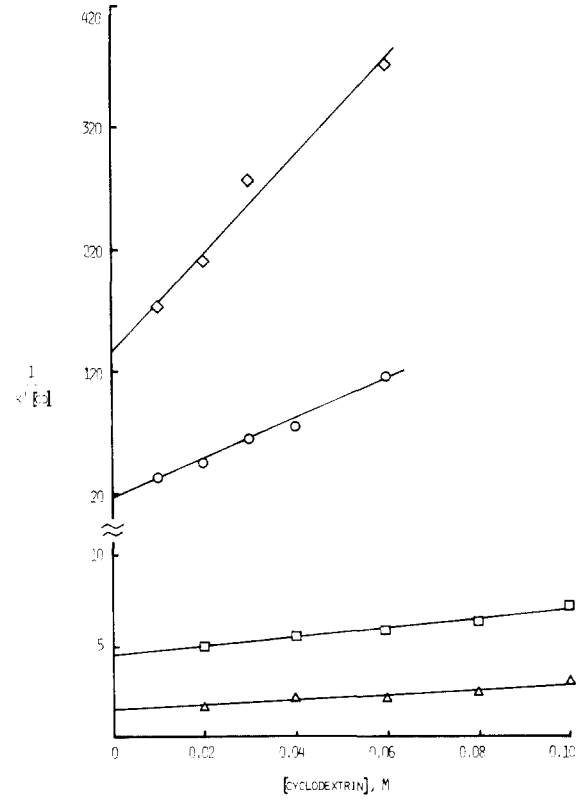

Figure 3. A direct determination of the second binding constant (K_2) of 2:1 cyclodextrin:substrate complexes can be obtained from plots such as these for *p*-nitroaniline (◇), 4,4′-biphenol (○), prostaglandin B_1 (□), and prostaglandin B_2 (△). Analogous plots of $1/k'[CD]$ vs. [CD] for 1:1 complexes produce downward curving lines of negative slope.

Table II. Cyclodextrin to Solute Stoichiometry and Binding Constants

compound	stoichiometry	K_1, M^{-1}	std dev[a]	K_2, M^{-1}	std dev[a]
prostaglandin B_1	2:1	144	6.5	7.3	0.4
prostaglandin B_2	2:1	95	4.5	6.2	0.3
4,4′-biphenol	2:1	300	15.1	102[b]	5.0
o-nitroaniline	1:1	23	1.0		
m-nitroaniline	1:1	73	3.2		
p-nitroaniline	2:1	430	20.0	32[b]	1.5

[a] All slopes and intercepts were determined by the method of least squares. The correlation coefficients of all plots were greater than 0.98. [b] Competitive indicator methods[23,24] also indicate secondary binding for these compounds.

one binds via hydrogen bonds (or other weak interactions) near the mouth of the other CD.

It is becoming increasingly evident that cyclodextrin inclusion complexation is not as simple as once believed. It is dangerous to assume a 1:1, 1:2, or 2:1 complex exists without some definitive experimental evidence. For example, this study has shown that two cyclodextrin molecules bind prostaglandin B_1 and B_2 and *p*-nitroaniline while earlier studies assumed 1:1 stoichiometries.[29-31] Obviously, this can significantly alter the interpretation of one's results in studies involving cyclodextrins. For example, rate constants could be significantly altered in going from a 1:1 to a 1:2 complex in catalysis studies involving cyclodextrins. Also the understanding of chiral recognition in cyclodextrin-based systems requires accurate information on both the stoichiometry and conformation of these complexes.

(29) Vekama, K.; Hirayama, F.; Ikeda, K.; Inaba, K. *J. Pharm. Sci.* **1977**, *66*, 706.

(30) Vekama, K.; Hirayama, F.; Irie, T. *Chem. Lett. (Jpn.)* **1978**, 661.

(31) Kawaguchi, Y.; Tanaka, M.; Nakae, M.; Funazo, K.; Shono, T. *Anal. Chem.* **1983**, *55*, 1852.

Potential Primary Pyrolysis Processes for Disilane

Mark S. Gordon,* Thanh N. Truong, and Elizabeth K. Bonderson

Contribution from the Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105. *Received June 17, 1985*

Abstract: Four competing unimolecular decomposition pathways for disilane are considered with use of MP4 energies obtained with an extended basis set and geometries obtained at the MP2/6-31G** computational level. The 1,1- and 1,2-eliminations of H_2 and the elimination of silylene to form silane all have similar endothermicities, but the very high activation energy for the 1,2-elimination eliminates this process as a significant contributor at low energies. If disilene is formed in the thermal decomposition of disilane, the more likely source is its higher energy isomer silylsilylene via a relatively low energy 1,2-hydrogen shift.

I. Introduction

In the pyrolysis of silane, both trisilane and tetrasilane are detected as final products.[1] An explanation proposed for the appearance of these species is that one of the primary products, silylene (SiH_2), inserts into the parent silane to form disilane. The latter then may itself lose molecular hydrogen to yield silylsilylene (1,1-elimination) or disilene (1,2-elimination). The first of these isomers has been implicated in the subsequent formation of trisilane, while the latter may be the origin of the observed tetrasilane.[1] Alternatively, disilene might be formed via a 1,2-shift from its isomer silylsilylene rather than by direct hydrogen elimination.

It appears to be generally accepted that the primary products in the pyrolysis of disilane result from the molecular elimination of hydrogen or silane.[2] Three such processes, reactions 1-3, are possible:

$$SiH_3—SiH_3 \rightarrow SiH_4 + SiH_2 \quad (1)$$

$$SiH_3—SiH_3 \rightarrow SiH_3—SiH + H_2 \quad (2)$$

$$SiH_3—SiH_3 \rightarrow SiH_2{=}SiH_2 + H_2 \quad (3)$$

$$SiH_3—SiH_3 \rightarrow SiH_3 + SiH_3 \quad (4)$$

In addition, one can imagine that the Si-Si homolytic cleavage (reaction 4) might be competitive. Of these four reactions, (1) appears to be the dominant primary process,[2] while (4) is less likely due to the 75 kcal/mol required to break the Si-Si single bond.[3] Detection of molecular hydrogen implicates reactions 2 and 3, but it is not clear which of these two reactions is more important. The least motion attack of H_2 on ethylene to form ethane is symmetry forbidden.[4] Because of this, the non-least-motion pathway has a substantial barrier. Even though disilene is nonplanar,[5] one expects a similarly large barrier for reaction 3. In addition to symmetry considerations, the four-center transition state across a rather long Si-Si bond will make delocalized bonding involving all four centers difficult. This should destabilize the transition state relative to the reactants and products. Because of the expected large barrier to the 1,2-elimination, the formation of disilene may well proceed primarily by isomerization from silylsilylene.

This work was initiated primarily to consider the relative thermodynamics and energy barriers for reactions 2 and 3. To place these calculations in the proper perspective, they are compared with reactions 1 and 4, The reverse of reaction 1 has earlier been shown[6] to occur with no barrier, and the same will certainly be true for reaction 4. Improved values for the thermodynamic energy differences for these reactions are presented below. To complete the investigation of the energetically most favorable means for forming disilene, the isomerization process involving the products of reactions 2 and 3 is considered as well.

The molecular and vibrational structure of disilane have been well characterized experimentally,[7] and several theoretical paper concerning this molecule have appeared as well.[8] The first

(1) Olbrich, G.; Potzinger, P.; Reimann, B.; Walsh, R. *Organometallics* **1984**, *3*, 1267.

(2) Dzarnoski, J.; Rickborn, S. F.; O'Neal, H. E.; Ring, M. A. *Organometallics* **1982**, *1*, 1217.

(3) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(4) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Germany, 1970.

(5) Cowley, A. H. *Polyhedron* **1984**, *3*, 389.

(6) Gordon, M. S.; Gano, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 5421.

(7) Bethke, G. W.; Wilson, E. B., Jr. *J. Chem. Phys.* **1957**, *26*, 1107. Beagley, B.; Conrad, A. R.; Freeman, J. M.; Monaghan, J. J.; Norton, B. G.; Holywell, G. C. *J. Mol. Struct.* **1972**, *11*.

(8) See, for example: Nicolas, G.; Barthelat, J. C.; Durand, P. *J. Am. Chem. Soc.* **1976**, *98*, 1346. Snyder, L. C.; Wasserman, Z. *Chem. Phys. Lett.* **1977**, *51*, 349. Mehandru, S. P.; Ray, N. K. *Indian J. Chem.* **1978**, *16A*, 1. Blustin, P. H.; Dacre, P. D.; Whittaker, C. G. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 982. Moskowitz, J. W.; Topiol, S.; Snyder, L. C.; Ratner, M. A. *Int. J. Quantum Chem.* **1981**, *19*, 131. Xu, J. H.; Mallow, J. V.; Ratner, M. A. *J. Phys. B* **1983**, *16*, 3863. Battistoni, C.; Lapiccirella, A.; Semprini, E.; Stefani, F.; Tomassini, N. *Nuovo Cimento Soc. Ital. Fis.* **1984**, *3D*, 663.

0002-7863/86/1508-1421$01.50/0