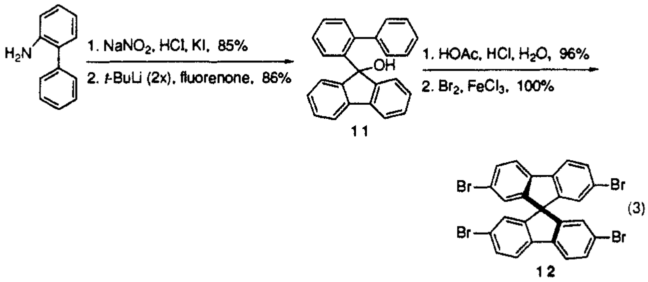
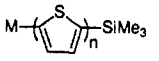
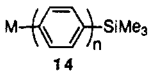
electronic architectural requirements. Conversion of 2-aminobiphenyl to the corresponding iodide under Sandmeyer[10] conditions followed by lithium halogen exchange and quenching with fluorenone afforded the alcohol **11**. Acid treatment to close the spiro system[11] followed by reaction with bromine and $FeCl_3$ gave the tetrabromide **12** in excellent yields (eq 3).[6] Bromination occurred only at the positions para to the second ring in the chain as one would expect by resonance stabilization arguments of the ionic intermediate. It is imperative that the bromination take place at the para position since a 4-substituted moiety is essential to afford a highly conducting system.[9]



With two key core units in hand, we then addressed methods to selectively and equally extend the chains in all four directions. Coupling **9** and **12** with **13** and **14**, respectively, using transition-metal catalysis[12] would allow for the selective introduction of a known number of units.[13] Additionally, the terminal trimethylsilyl group in **13** and **14** would allow for selective bromination at those sites and, hence, a position for further coupling if necessary.[8a] Accordingly, treatment of **9** with **13** ($M = Bu_3Sn$, $n = 1$) in the presence of catalytic $Pd(PPh_3)_4$ afforded **15** in 41% yield. Likewise, treatment of **12** with **14** ($M = ClZn$, $n = 1$) under similar catalytic conditions afforded **16** in 40% yield.[6] Use of 3-substituted thiophenes for connection to both **9** and **12** is also being investigated to help in solubilizing these systems.[13,14]

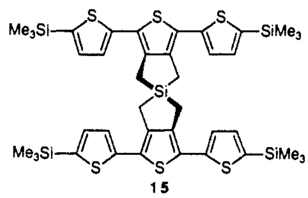


13



14

M= R_3Sn, XZn, XMg



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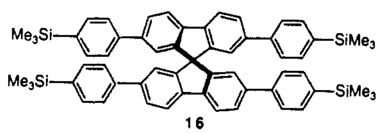

16

Clearly, the efficiency of these coupling reactions must be optimized and the chain lengths further extended. However, these synthetic approaches demonstrate the power of modern synthetic methods to allow for the construction of macromolecules with the extremely specific architectural requirements necessary for the construction of the future molecular electronics based computing machine.

Acknowledgment. This research was funded by the Department of the Navy, Office of the Chief of Naval Research, Young Investigator Program (N00014-89-J-3062), the National Science Foundation EPSCoR program (RII-8922165), and the University of South Carolina Venture Fund.

Supplementary Material Available: Detailed synthetic procedures for compounds **7-9**, **11**, **12**, **15**, and **16** (6 pages). Ordering information is given on any current masthead page.

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[9] For a discussion of polyphenylene, see: (a) Elsenbaumer, R. L.; Shacklette, L. W. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. For related syntheses, see: (b) Yamamoto, T.; Hayashi, Y.; Tamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091. (c) Kovacic, P.; Oziomek, J. *J. Org. Chem.* **1964**, *29*, 100.

[10] Heaney, H.; Millar, I. T. *Org. Synth.* **1960**, *40*, 105.

[11] Clarkson, R. G.; Gomberg, M. *J. Am. Chem. Soc.* **1930**, *52*, 2881.

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[13] For a discussion of polythiophene and its derivatives, see: Tourillon, G., in ref 9a.

[14] for a discussion of mixed thiophene/phenylene semiconductors, see, for example: Pelter, A.; Maud, J. M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.* **1989**, *30*, 3461.

C-H Bond Activation as the Initial Step in the Co^+-Mediated Demethanation of Propane: The Critical Role of Angular Momentum at the Rate-Limiting Transition State

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Exothermic reactions of transition-metal ions with alkanes have in many instances been shown to be facile in the gas phase.[1] Reactions mainly result in the loss of molecular hydrogen and small alkanes to yield metal ion-olefin complexes. A variety of experimental techniques have provided thermochemical, kinetic, dynamic, and mechanistic information for these reactions, with an important focus being the identification of the initial activation step. The question of C-H versus C-C bond activation as the initial step in the formation of C-C bond cleavage products has yet to be resolved.[2]

We have measured reaction cross sections and kinetic energy release distributions for the exothermic reactions of Co^+ with propane, propane-2-d_1, propane-$2,2$-d_2, propane-$1,1,1$-d_3, propane-$1,1,1,3,3,3$-d_6, and propane-d_8. Both dehydrogenation and demethanation pathways are observed in all systems, although the emphasis here is on the demethanation reaction. Our observations demonstrate that this system is sensitive to the small perturbations induced by isotopic substitutions, and these provide insight into the fundamental question of initial C-H versus C-C bond activation for the demethanation process. Many exothermic gas-phase ion-molecule reactions occur near the collision rate at thermal energy due to the electrostatic attraction between the ion and the neutral.[3] In these cases the chemical activation provided

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[†] Contribution No. 8113.

[1] For recent reviews see: (a) Allison, J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1986; pp 34 and 628 and references therein. (b) Armentrout, P. B. In *Gas Phase Inorganic Chemistry*; Russel, D., Ed.; Plenum: New York, 1989; p 1.

[2] The two possibilities usually considered for alkane elimination involve insertion into a C-H bond followed by a β-alkyl shift and insertion into a C-C bond followed by a β-hydrogen shift. (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197. (c) Tonkyn, R.; Ronan, M.; Weisshaar, J. C. *J. Phys. Chem.* **1988**, *92*, 92. (d) Georgiadis, R.; Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 4251. (e) Schwarz, H. *Acc. Chem. Res.* **1989**, *22*, 282.

[3] Ikezoe, Y.; Matsuoka, S.; Takebe, M.; Viggiano, A. *Gas-Phase Ion-Molecule Reaction Rate Constants Through 1986*; Maruzen: Japan, 1987.

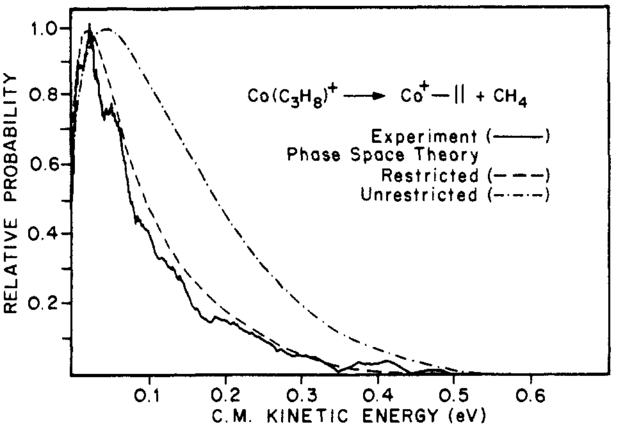

Figure 1. Experimental and theoretical kinetic energy release distributions for metastable loss of CH_4 from nascent $Co(C_3H_8)^+$ collision complexes. The "unrestricted" phase space theory curve assumes the entrance and exit channel contain only orbiting transition states and that there are no tight transition states in between that affect the dynamics. The "restricted" phase space theory calculation includes a tight transition state for insertion into a C–H bond located 0.11 eV below the asymptotic energy of the reactants. Collisions that surmount the centrifugal barrier are reflected at the tight transition state above a particular orbital angular momentum. This restricts the range of angular momentum available to the products and reduces the kinetic energy release.

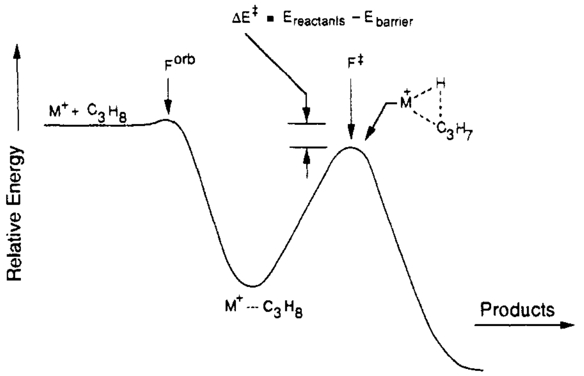

Figure 2. A schematic reaction coordinate diagram for insertion of Co^+ into a C–H bond of C_3H_8. The fluxes through the orbiting and tight transition states are depicted as F^{orb} and $F^{\ddagger}$, respectively.

by the attractive interaction is sufficient to overcome intrinsic barriers that may be associated with insertion into a C–H or C–C bond. Our cross-section measurements show that the reaction of Co^+ with propane is inefficient, however, occurring at only 13% of the collision limit at low kinetic energy. For Co^+ reacting with C_3D_8 the total cross section is even lower, reduced by nearly a factor of 3 relative to C_3H_8.

In earlier studies[4] we have demonstrated that kinetic energy release distributions for alkane loss processes can be successfully modeled using what we will refer to as unrestricted statistical phase space theory.[5-7] This analysis yields reaction exothermicities and hence metal–ligand bond dissociation energies. Experimental and theoretical kinetic energy release distributions for CH_4 loss are shown in Figure 1. The Co^+–ethene bond energy has been separately determined[4] and is not a variable in the phase space calculations. With use of this known bond energy, the disagreement of the calculated and experimental distributions is substantial with the experimental distribution much narrower than expected statistically (Figure 1). The inefficiency of the reaction, the isotope effect, and the translationally cold kinetic energy release distribution can be accommodated by the following model.

A schematic reaction coordinate diagram is shown in Figure 2 where an initial electrostatic potential well is followed by a tight transition state that involves C–H insertion and restricts the flux out to products. The metal ion reacts with propane forming an electrostatic ion-molecule complex. This complex can either go through a tight transition state and proceed to products or go back through the orbiting transition state to reactants.[8] The reaction can be schematically written as in eq 1. The corresponding rate

$$M^+ + C_3H_8 \underset{k_{orb}}{\overset{k_{collision}}{\rightleftharpoons}} [M(C_3H_8)^+]^* \xrightarrow{k_\ddagger} \text{products} \qquad (1)$$

constant for product formation is given by eq 2, where $k_{collision}$ is

$$k_{products} = k_{collision}\left(\frac{k_\ddagger}{k_{orb} + k_\ddagger}\right) \qquad (2)$$

the Langevin collisional rate constant[9] and k_{orb} and $k_\ddagger$ are unimolecular rate constants defined in reaction 1. The reaction probability, $k_{products}/k_{collision}$, was calculated as a function of $\Delta E^\ddagger$, the energy of the rate-limiting transition state relative to the asymptotic energy of the reactants. As $\Delta E^\ddagger \rightarrow 0$, $k_{products}/k_{collision} \rightarrow 0$, and essentially no products are observed. As the barrier decreases relative to the reactant energy, the rate of product formation increases until the Langevin limit is attained (where reaction occurs on every collision). The cross-section measurements indicate a reaction efficiency ($k_{products}/k_{collision}$) of 13 ± 5%, which corresponds to $\Delta E^\ddagger = 0.11 \pm 0.03$ eV.

The same model was applied to the isotopically labeled species. The maximum change in the transition-state energy upon deuteration is the zero-point energy difference between C–H and C–D bonds. With use of the maximum difference of 0.047 eV, the theoretical reaction cross section for C_3D_8 relative to C_3H_8 decreases by a factor of 2.6 ± 0.4,[10] in very good agreement with the experimental value of 2.8 ± 0.8.[11] This agreement indicates that the C–H (C–D) bond is completely broken in the transition state.[12]

The theoretical kinetic energy release distribution using restricted phase space theory calculations, which include the tight transition state for C–H bond activation located 0.11 eV below the reactant energy, gives a very good fit with the experiment (Figure 1). As the barrier is decreased relative to the reactant energy, the distribution broadens until the unrestricted phase space theory limit is attained. The average kinetic energy released reduces from 0.15 eV (assuming no rate-limiting barrier) to 0.10 eV (including the rate-limiting transition state).

The kinetic energy release distribution for an exothermic process with no reverse barrier is determined mainly by the potential energy surface in the region associated with product formation, with angular momentum constraints being provided by the orbiting transition state encountered during the initial interaction.[6,7] In the present case, more restrictive angular momentum constraints arise from a tight transition state further along the reaction coordinate.[13] It is the position and energy of this rate-limiting

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(4) (a) van Koppen, P. A. M.; Bowers, M. T.; Beauchamp, J. L.; Dearden, D. V. Contribution for ACS Symposium Volume, Bond Energies and the Thermodynamics of Organometallic Reactions (in press). (b) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; van Koppen, P. A. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 1.

(5) "Unrestricted" versus "restricted" phase space theory is defined in the caption for Figure 1.

(6) (a) Pechukas, P.; Light, J. C.; Rankin, C. J. *Chem. Phys.* **1966**, *44*, 794. (b) Nikitin, E. *Theor. Exp. Chem.* (*Engl. Transl.*) **1965**, *1*, 285.

(7) (a) Chesnavich, W. J.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 8301. (b) Chesnavich, W. J.; Bowers, M. T. *J. Chem. Phys.* **1978**, *68*, 901. (c) Chesnavich, W. J.; Bowers, M. T. *Prog. Reaction Kinet.* **1982**, *11*, 137.

(8) At higher pressures collisional stabilization of the complex is observed in the cross-section measurements and in ref 2c.

(9) Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294.

(10) The parameters used in the calculations including vibrational frequencies and rotational constants were taken from the literature where possible. When these parameters were not available, reasonable estimates were made. These estimated parameters were varied over the entire range of values that are physically reasonable. The uncertainty in the calculated isotope effect of the cross section reflects the variation in these parameters.

(11) These considerations have been for propane and propane-d_8. The other isotopic variants also support the proposed model and will be discussed more fully in a complete account of this work.

(12) A similar effect has been observed in gas-phase base-induced elimination reactions: Bierbaum, V. M.; Filley, J.; DePuy, C. H.; Jarrold, M. F.; Bowers, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2818.

(13) This occurrence may actually be more common than generally envisioned (see ref 10).

transition state that makes the propane system so sensitive to small perturbations such as isotope and angular momentum effects. Statistical phase space theory can successfully model the reaction cross section, the isotope effect, and the kinetic energy release distribution if C–H rather than C–C bond activation is assumed to be the initial and rate-limiting step for demethanation of propane.[14]

Acknowledgment. The support of the National Science Foundation under Grants CHE88-17201 (M.T.B.), CHE87-11567 (J.L.B.), and CHE87-96289 (P.B.A.) is gratefully acknowledged. J.L.B. also thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, and J.B.-L. thanks the National Science Foundation for a postdoctoral fellowship. In addition, we gratefully acknowledge helpful discussions with Drs. Martin Jarrold and Marina Rincon regarding the theoretical calculations.

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(14) At higher kinetic energies reaction cross-section data suggest that C–C bond insertion processes may become accessible.

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n-Pentenyl Glycosides as Efficient Synthons for Promoter-Mediated Assembly of N-α-Linked Glycoproteins[1]

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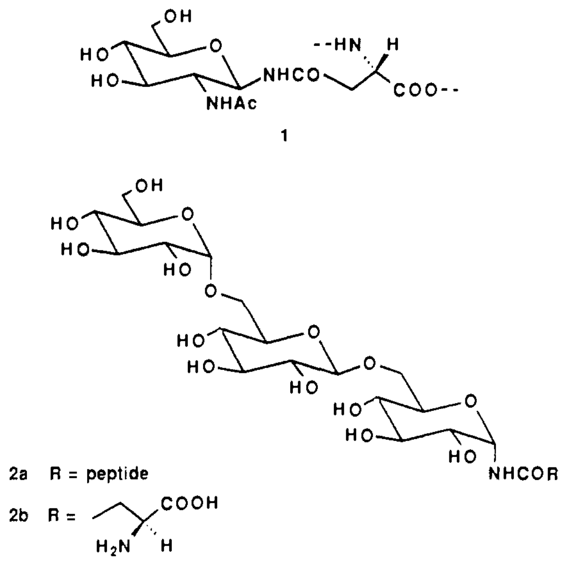
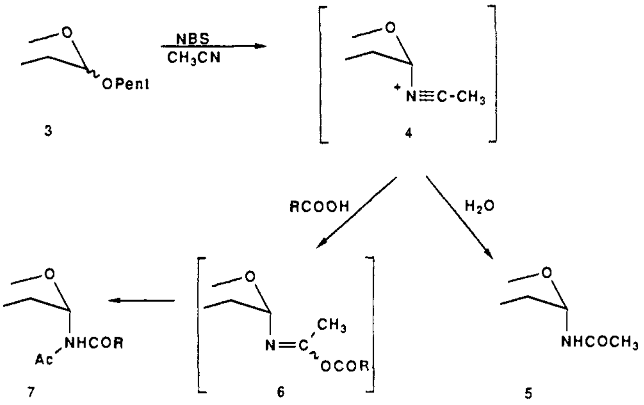
It is now well established that glycoproteins are among some of nature's most widespread bio-regulators, being implicated in a wide variety of vital life processes,[3] and the key roles played by the carbohydrate components have been clearly established.[4] Largely because of modern spectroscopic techniques, daunting problems surrounding elucidation of their structures have been overcome, and their composition, once thought to be hopelessly chaotic, is now known to show certain basic features. Thus, 2-acetamido-1-*N*-(L-aspart-4-oyl)-2-deoxy-*β*-D-glucopyranosylamine **1** is the common link between the oligosaccharide and polypeptide components,[3a,5] and a variety of synthetic protocols for this N-acyl-*β*-linkage have been developed.[6,7] The structural elucidation of the nephritogenic glycopeptide **2a**,[8] isolated from rat glomerular basement membrane,[9] was therefore noteworthy in that it contained an *α*-D-glucopyranose as the glycan "linker" to the amide group of L-asparagine.[10]

Chart I



Scheme I



In this communication, we report a synthesis of the crucial segment of **2b**,[11] which demonstrates (a) a novel route to the construction of such *α*-linked glycopyranosylamides and (b) the use of *N*-iodosuccinimide and trifluoromethanesulfonic acid for reacting "disarmed"[12] *n*-pentenyl glycosyl donors without breaking covalent bonds.[24]

The inspiration for tackling this project came from our recent studies on the oxidative hydrolysis of restrained *n*-pentenyl glycosides in which *α*-*N*-acetyl glycopyranosyl amines (e.g., **5**) were obtained as major products.[13] Their formation required the

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(1) This work was supported by grants from the National Science Foundation (CHE 8703916), and Glycomed, Incorporated (Hayward, CA).

(2) (a) A.J.R. is grateful to the Science and Engineering Research Council (UK) for a NATO Postdoctoral Research Fellowship. (b) Present address: IFM/KEMI, University of Linkoping, S-581 83 Linkoping, Sweden.

(3) For reviews see: (a) Montreuil, J. In *Comprehensive Biochemistry*; Neuberger, A., van Deenen, L. L. M., Eds.; Elsevier: Amsterdam, 1982; Vol. 19BII, p 1. (b) Schwarz, R. T.; Datema, R. *Adv. Carbohydr. Chem. Biochem.* **1982**, *40*, 287. Olden, K.; Bernard, B. A.; Humphries, M. J.; Yeo, T.; Yeo, K.; White, S. L.; Newton, S. A.; Bauer, H. C.; Parent, J. B. *Trends Biochem. Sci. Pers, Ed.* **1985**, *10*, 78. (c) Fukuda, M. *Biochim. Biophys. Acta* **1984**, *780*, 119. (d) Springer, G. F.; Desai, P. R.; Murthy, M. S.; Scanlon, E. F. *ACS Symp. Ser.* **1978**, *80*, 311. (e) Ofek, I.; Beachey, E. H.; Sharon, N. *Trends Biochem. Sci. Pers. Ed.* **1978**, *3*, 159. (f) Feizi, T. *Nature* (*London*) **1985**, *314*, 53.

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(5) Johansen, P. G.; Marshall, R. D.; Neuberger, A. *Biochem. J.* **1961**, *78*, 518.

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(10) It is not clear from ref 8a whether L-asparagine or L-glutamine is the glycan–protein linkage. We have decided to adopt the former in developing our methodology given it is the one more usually found in glycopeptides.

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