

ketone (0.03 mmol),  $\text{NaIO}_4$  (0.75 mmol), and  $\text{RuCl}_3(\text{H}_2\text{O})_3$  (0.002 mmol) was stirred in  $\text{CCl}_4\text{-H}_2\text{O-CH}_3\text{CN}$  (2:1:2) (1.0 mL) for 36-48 h at room temperature. The resulting mixture was diluted with ether and the organic layer was dried over anhydrous  $\text{MgSO}_4$ . Removal of the solvents followed by separation with column chromatography gave the corresponding diketone. **1-(3-Oxocyclohexyl)-3-hexanone**: bp 145 °C (bath temperature) (20 mmHg); IR (neat) 1700; NMR ( $\text{CCl}_4$ ) 0.85 (t,  $J = 7$  Hz, 3 H), 1.31-2.08 (m, 9 H), 2.33 (m, 8 H). **1-(3-Oxocyclohexyl)-5-methyl-3-hexanone**: bp 150 °C (bath temperature) (20 mmHg); IR (neat) 1700; NMR ( $\text{CCl}_4$ ) 0.98 (d,  $J = 7$  Hz, 6 H), 1.33-1.66 (m, 8 H), 2.31 (m, 8 H).

**Lewis Acid Mediated Reaction of Bis-Silyl Enol Ether 7c with an Aromatic Acetal.** To a dichloromethane (0.2 mL) solution of an aromatic acetal (0.08 mmol) and  $\text{SnCl}_4$  (0.08 mmol) was added a dichloromethane (0.1 mL) solution of 3-(*tert*-butyldimethylsiloxy)-1-[3-(trimethylsiloxy)-2-cyclohexenyl]-2-decene (**7c**) (0.08 mmol) at -70 °C and the mixture was stirred for 1 h at that temperature. Then the reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$  solution and the aqueous layer was extracted with ether. The combined extracts were washed with saturated aqueous NaCl solution and dried over anhydrous  $\text{MgSO}_4$ . Removal of the solvents followed by separation with silica gel column chromatography afforded the corresponding ring-closure product.

**2-(1-Octanoyl)-3-phenyl-4,5,6,7-tetrahydro-4-indanone**: yield 65%; IR (neat) 1700; NMR ( $\text{CCl}_4$ ) 0.82 (t,  $J = 7$  Hz, 3 H), 1.12-1.43 (m, 17 H), 1.59 (m, 1 H), 1.89-2.43 (m, 6 H), 7.12-7.16 (m, 5 H). **2-(1-Octanoyl)-3-ethyl-3-phenyl-4,5,6,7-tetrahydro-4-indanone**: yield 62%; IR (neat) 1700; NMR ( $\text{CCl}_4$ ) 0.89 (t,  $J = 7$  Hz, 6 H), 1.10-1.50 (m, 19 H), 1.92-2.47 (m, 6 H), 7.21 (bs, 10 H).

**Fluoride-Induced Cyclization of 6-Siloxy-2,5-dienoic Ester 10.** A THF (0.1 mL) solution of methyl 6-(*tert*-butyldimethylsiloxy)-2,5-tridecadienoate (**10**) (70.8 mg, 0.25 mmol) was added to a THF (0.2 mL) solution of tetrabutylammonium fluoride (97.9 mg, 0.38 mmol) at -70 °C. After the mixture was stirred for 1 h at -70 °C, for 1 h at -40 °C, and then for 30 min at 0 °C, it was quenched with 1 N HCl. The aqueous layer was extracted with ether and the combined extracts were dried over anhydrous  $\text{MgSO}_4$ . Removal of the solvents followed by purification with column chromatography gave 2-(methoxycarbonylmethyl)cyclopropyl heptyl ketone (**11**) (37.2 mg, 62%); IR (neat) 1720, 1700; NMR ( $\text{CCl}_4$ ) 0.90 (t,  $J = 7$  Hz, 3 H), 1.10-1.28 (m, 13 H), 1.95-2.10 (m, 5 H), 3.56 (s, 3 H).

**Reaction of 4-Ethyl-3-(trimethylsiloxy)-2-hexenylmagnesium Bromide with Cyclohexanone.** 2-Ethylbutyryltrimethylsilane (0.1 mmol) was added to a THF solution of vinylmagnesium bromide (0.1 mL of a 1.0 M solution, 0.1 mmol) at 0 °C and the solution was stirred for 10 min at room temperature. To the resulting solution was added a THF (0.2 mL) solution of cyclohexanone (0.1 mmol) at 0 °C and the mixture was stirred for 10 h at room temperature. The solution was then quenched with saturated aqueous NaCl solution and the aqueous layer was extracted with ether. After the combined extracts were dried over anhydrous  $\text{MgSO}_4$ , removal of the solvents followed by separation with silica gel column chromatography afforded 1-[3-(4-ethyl-3-trimethylsiloxy-1-hexenyl)cyclohexan-1-ol (16.6 mg, 56%) and 1-(4-ethyl-3-trimethylsiloxy-2-hexenyl)cyclohexan-1-ol (3.4 mg, 11%). **1-[3-(4-Ethyl-3-trimethylsiloxy-1-hexenyl)cyclohexan-1-ol**: IR (neat) 3350, 1240, 840; NMR ( $\text{CCl}_4$ ) 0.02 (s, 9 H), 0.73 (t,  $J = 7$  Hz, 6 H), 1.09-1.47 (m, 15 H), 4.66 (dd,  $J = 17$  and 2 Hz, 1 H), 4.68 (dd,  $J = 10$  and 2 Hz, 1 H), 5.38 (dd,  $J = 17$  and 10 Hz, 1 H). **1-(4-Ethyl-3-trimethylsiloxy-2-hexenyl)cyclohexan-1-ol**: IR (neat) 3350, 1250, 840; NMR ( $\text{CCl}_4$ ) 0.10 (s, 9 H), 0.77 (t,  $J = 7$  Hz, 6 H), 1.13-1.44 (m, 14 H), 1.93 (d,  $J = 7$  Hz, 2 H), 2.52 (m, 1 H), 4.28 (t,  $J = 7$  Hz, 1 H).

**Reaction of 4-Ethyl-3-(trimethylsiloxy)-2-hexenylmagnesium Bromide with Benzoyl Chloride.** To a THF solution of the hexenylmagnesium bromide (0.1 mmol) generated as above was added a THF (0.2 mL) solution of benzoyl chloride (0.1 mmol) at -70 °C, and the mixture was stirred for 1 h at -70 °C and then for 1 h at 0 °C. The solution was diluted with ether and quenched with saturated aqueous  $\text{NaHCO}_3$  solution. The aqueous layer was extracted with ether and the combined extracts were dried over anhydrous  $\text{MgSO}_4$ . Removal of the solvents followed by separation with silica gel column chromatography afforded 3-benzoyl-4-ethyl-3-(trimethylsiloxy)-1-hexene (29.9 mg, 97%); IR (neat) 1690, 1240, 840; NMR ( $\text{CCl}_4$ ) 0.02 (s, 9 H), 0.80 (t,  $J = 7$  Hz, 6 H), 1.33-2.27 (m, 5 H), 5.40 (dd,  $J = 17$  and 2 Hz, 1 H), 5.42 (dd,  $J = 9$  and 2 Hz, 1 H), 5.86 (dd,  $J = 17$  and 9 Hz, 1 H), 7.20-7.34 (m, 3 H), 7.61-7.97 (m, 2 H).

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## Dimerization of the [8]Annulene Anion Radical

Gerald R. Stevenson\* and Mark A. Nebgen

Contribution from the Department of Chemistry, Illinois State University, Normal, Illinois 61761. Received December 10, 1984

**Abstract:** Dilute solutions of the anion radical of [8]annulene ( $[8]^-$ ) in hexamethylphosphoramide, where ion association is absent, dimerize, resulting in the formation of the [16]annulene anion radical. This disappearance of  $[8]^-$  follows second-order kinetics (rate =  $-d[[8]^-]/dt = k[[8]^-]^2$ ) with a rate constant of  $7.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  at 30 °C. However, the rate of formation of the [16]annulene anion radical is much slower than the rate of disappearance of  $[8]^-$ . This is interpreted in terms of a polymerization reaction.

A number of aromatic hydrocarbon cation radicals ( $\text{R}^+$ ) react spontaneously with neutral molecule (R) to form the dimer cation radical ( $\text{R}_2^+$ ).<sup>1</sup> On the other hand, it has been predicted that analogous anion radical dimers ( $\text{R}_2^-$ ) would be unstable relative to the monomer anion radical and neutral molecule.<sup>2,3</sup> Indeed, hydrocarbon dimer anion radicals have yet to be observed.<sup>2</sup>

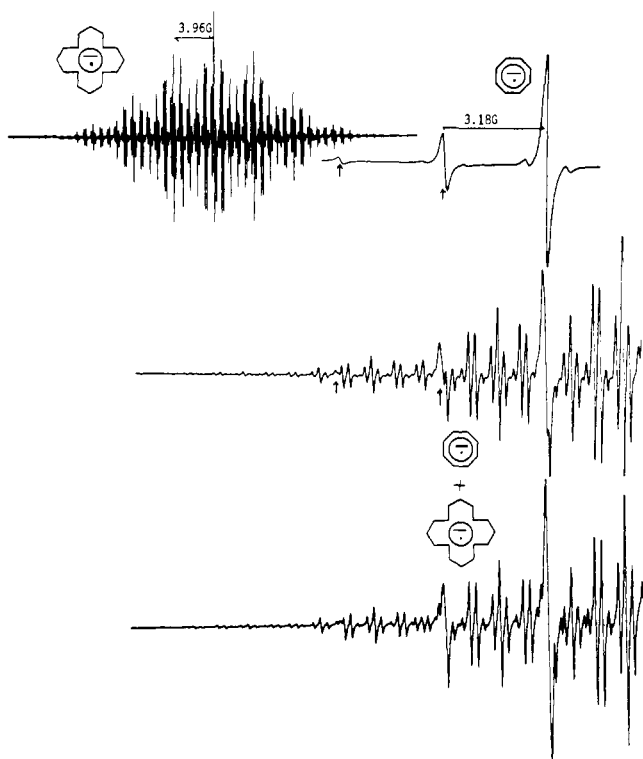
However, Williams and co-workers<sup>4</sup> did find that a frozen solution of the anion radical of tetrafluoroethylene in methyltetrahydrofuran (MTHF) readily reacts with neutral  $\text{C}_2\text{F}_4$  to form the anion radical of perfluorocyclobutane. Their work<sup>4</sup> represents the only documented case for the formation of a dimer anion radical from an olefinic anion radical. The only other dimer anion radicals have been those of the nitriles.<sup>4</sup> Theory suggests that the forbidden ( $2 + 2$ ) suprafacial process, which is forbidden for the  $\pi-\pi^*$  cycloaddition of ethylene,<sup>5</sup> becomes allowed for the Williams

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(2) (a) Brocklehurst, B. *J. Phys. Chem.* **1971**, *75*, 1177; (b) Itoh, M. *J. Am. Chem. Soc.* **1970**, *92*, 7239.

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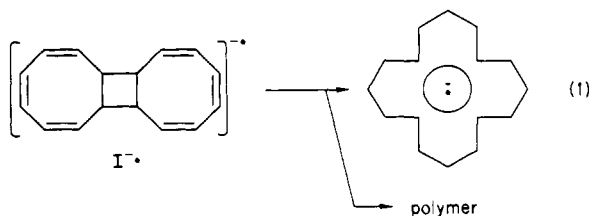
(4) McNeil, R. I.; Shiotani, M.; Williams, F.; Yim, M. B. *Chem. Phys. Lett.* **1977**, *51*, 438.



**Figure 1.** ESR spectra taken at various times after the formation of a 0.1 M [8]annulene solution in HMPA in the presence of the anion radical. The spectrum in the upper left-hand corner represents that taken after 2 weeks. It is due to the anion radical of [16]annulene with only a trace of the [8]annulene anion radical present. The top spectrum on the right is that taken immediately after the formation of the anion radical solution. Only the first three lines of [8]<sup>-</sup> are shown (the first two are marked with arrows). The middle spectrum was obtained from the same solution 2 days later. It shows the presence of a considerably quantity of [16]<sup>2-</sup>. The bottom spectrum is a computer simulation of the spectrum of a 5:1 [8]<sup>-</sup>/[16]<sup>2-</sup> mixture of anion radicals. The <sup>13</sup>C lines were not included in the simulation.

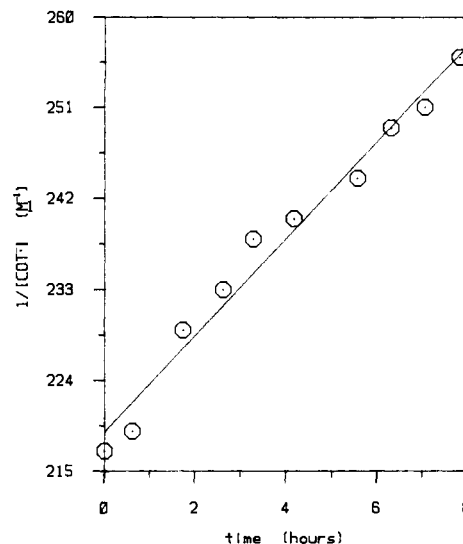
reaction due to the perturbation of the LUMO by the fluorines.<sup>4</sup> We now wish to report the generation of the anion radical of [16]annulene ([16]<sup>2-</sup>) directly from that of [8]annulene ([8]<sup>-</sup>). This reaction represents the first example of the formation of a hydrocarbon anion radical dimer.

The anion radical of [16] was first generated by Schroder and co-workers<sup>6</sup> via the reduction of the neutral molecule with alkali metal. Later Concepcion<sup>7</sup> and Vincow found that this anion radical could be generated without the laborious synthesis of neutral [16] by simply reducing the (2 + 2) dimer of [8] in THF or in hexamethylphosphoramide (HMPA) (reaction 1). However, it has been pointed out that the reaction to produce [16]<sup>2-</sup> is not quantitative and a considerable amount of polymer is produced.<sup>8</sup>



## Results and Discussion

The reduction of COT (0.1–1 M) in HMPA with a very deficient (by at least 2 orders of magnitude) amount of sodium metal



**Figure 2.** Second-order plot of  $1/[8]^{2-}$  vs. time in hours at 45 °C. The rate constants for reaction 1 at various temperatures were taken from similar plots generated from the same anion radical solution. Using these same data to generate a plot of  $\ln(\text{rate})$  vs.  $\ln[[8]^{2-}]$  yields a straight line with a slope of  $2.1 \pm 0.3$ . These two plots indicate that the reaction is second order in [8]<sup>-</sup>.

results in a solution that yields the familiar nine-line ESR spectrum of the anion radical of [8]. After several hours at 25 °C, the ESR spectrum of this same solution shows the presence of the anion radical of [16] (Figure 1). Over a period of several days, the anion radical of [8] is gradually replaced with that of [16] (Figure 1). This reaction does not take place when THF serves as the solvent, and solutions of the [8]annulene anion radical can be kept for years at room temperature without noticeable decomposition. As ion association involving both the anion radical and dianion of [8] is present in THF,<sup>9</sup> we initially thought that this ion association must somehow "protect" the anion radical from forming [16]<sup>2-</sup> and that [16]<sup>2-</sup> resulted from the reaction of the anion radical of [8] with neutral [8] in a manner that is analogous to formation of  $C_4F_8^{2-}$  from  $C_2F_4^-$  and  $C_2F_4$ . In HMPA there is no ion association involving the dianion when either  $Na^+$  or  $K^+$  serves as the cation.<sup>10</sup> However,  $K^+$  is known to form ion pairs with the [8]annulene dianion.<sup>10</sup>

The addition of  $Na^+$  or  $K^+$ , as the iodide salts, to the HMPA solutions results in an increase in both the rate of decrease in the [8]<sup>-</sup> concentration and the rate of increase in the concentration of [16]<sup>2-</sup>. This augmentation of the rate must be due to a Debye–Hückel salt effect, since  $Na^+$  will not form ion pairs with [8]<sup>-</sup>, [8]<sup>2-</sup>, [16]<sup>2-</sup>, or [16]<sup>2-</sup>.<sup>11</sup> The rate increase with increasing ionic strength of the solution strongly suggests that the two reacting species are charged.

The salt effect upon the reaction suggests that the order in the neutral molecule should be zero in contrast to the formation of  $C_4F_8^{2-}$ . Experiments carried out by keeping the [8]annulene anion radical concentration constant but varying the neutral molecule concentration showed no variation of the rate of reaction. Further, solutions containing only the dianion of [8]annulene did not exhibit any decrease in the intensity of the NMR signal for [8]<sup>2-</sup> over a period of several weeks at 25 °C. Thus, neither the neutral molecule nor the dianion of [8] is involved in the rate-determining step of the reaction.

To ascertain the order of the reaction in terms of the anion radical, we utilized the dual-cavity ESR technique to monitor the concentration of [8]<sup>-</sup> during the course of the reaction. Plots of  $\ln(\text{rate})$  (rate = the rate of decrease in the concentration of [8]<sup>-</sup>) vs.  $\ln[[8]^{2-}]$  are linear and have a slope of  $2.1 \pm 0.1$ . This means

(5) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 2046.  
 (6) Oth, J. F. M.; Bauman, H.; Giles, J. M.; Schroder, G. *J. Am. Chem. Soc.* **1972**, *94*, 3498.

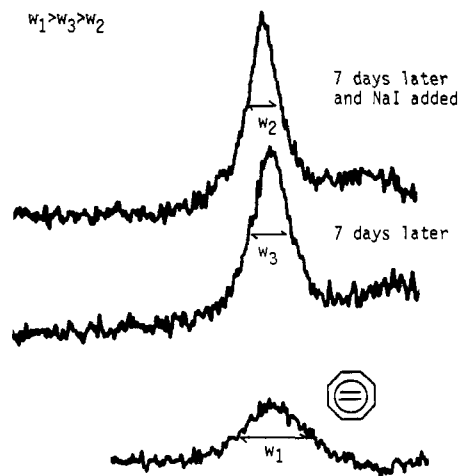
(7) Concepcion, J. G.; Vincow, G. *J. Phys. Chem.* **1975**, *79*, 2037.

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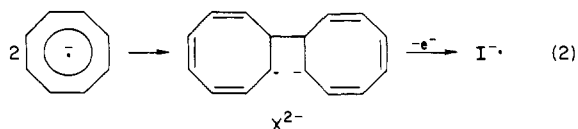
(10) Weidrich, C. R.; Catlett, D. L.; Sedgwick, J. B.; Stevenson, G. R. *J. Phys. Chem.* **1983**, *87*, 578.

(11) Stevenson, G. R.; Forch, B. E. *J. Phys. Chem.* **1981**, *85*, 378.



**Figure 3.**  $^1\text{H}$  NMR spectrum of  $[\text{8}]^{2-}$  in the presence of  $[\text{8}]^{\cdot-}$  in HMPA at  $35^\circ\text{C}$ . The bottom spectrum was recorded 5 min after the formation of the solution, and the upper spectra were recorded 7 days later. Note the narrower lines in the upper spectra. The top spectrum was taken from the same solution but with 0.03 M added NaI. The added  $\text{Na}^+$  and  $\text{I}^-$  ions increase the rate of anion radical dimerization, resulting in further narrowing of the NMR line.

that the primary step is simply the dimerization of the [8]annulene anion radical (reaction 2). If a dimerization of  $[\text{8}]^{\cdot-}$  is, indeed,

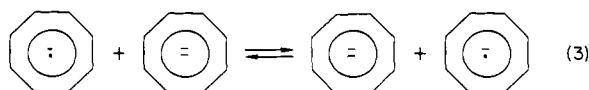


the initial step, a plot of  $1/[[\text{8}]^{\cdot-}]$  vs. time should be linear, and the slope of the resulting line will represent the second-order rate constant for reaction 2. Such plots are linear and yield rate constants of  $(1.33 \pm 0.07) \times 10^{-4}$ ,  $(7.5 \pm 0.1) \times 10^{-5}$ ,  $(6.7 \pm 0.8) \times 10^{-6}$ , and  $3.7 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$  at 45, 30, 10, and  $0^\circ\text{C}$ , respectively (Figures 2 and 3).

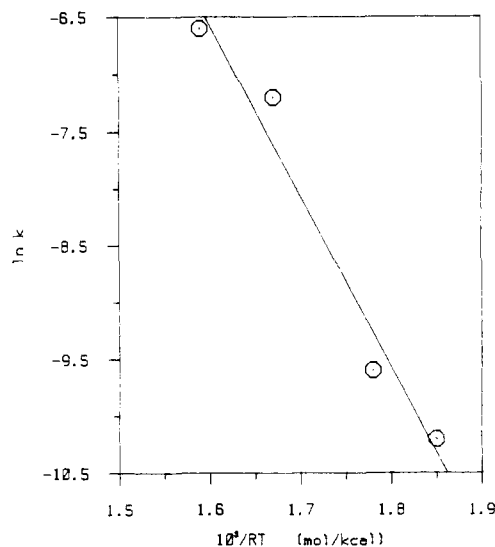
It has been observed that neutral [8]annulene will very rapidly extract an electron from most dianions and anion radicals.<sup>11</sup> Thus, the dimer dianion ( $\text{x}^{2-}$ ) would be expected to yield an electron to [8] at a rate that is at least 6 orders of magnitude greater than the dimerization of  $[\text{8}]^{\cdot-}$ . This dimer can then close to form  $\text{I}^{\cdot-}$ , which is known to result in both the formation of polymeric material and the anion radical of [16].<sup>7,8</sup>

The rate of increase in the [16]annulene anion radical concentration is about 10 times slower (this varies considerably with the temperature) than the rate of decrease in the concentration of the [8]annulene anion radical ( $-\text{d}[[\text{8}]^{\cdot-}]/\text{d}t \approx 10(\text{d}[\text{16}]^{\cdot-})/\text{d}t$ ). This observation confirms the fact that most of the dimerizations of  $[\text{8}]^{\cdot-}$  do not lead to the formation of  $[\text{16}]^{\cdot-}$ .

The decrease in the concentration of  $[\text{8}]^{\cdot-}$  with time results in a decrease in the [8]annulene dianion concentration also. Thus, not only does the signal intensity for  $[\text{8}]^{\cdot-}$  decrease, but the lines become narrower. The relatively broad ESR lines observed for  $[\text{8}]^{\cdot-}$  are due to the fast electron transfer between the dianion and anion radical (reaction 3).<sup>12</sup> The line-narrowing effect must be



due to the decrease in the rate of this electron-exchange reaction (3). If this is the case, a similar line narrowing should be observed in the proton NMR of  $[\text{8}]^{2-}$ . Figure 4 clearly shows how the single

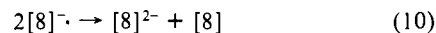
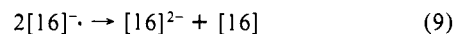
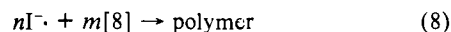
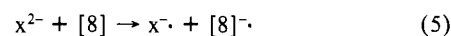


**Figure 4.** Plot of  $\ln$  (second-order rate constant) vs.  $10^3/RT$ . The slope of this line yields an energy of activation of  $15 \pm 1.7 \text{ kcal/mol}$  and an entropy of activation of  $-26 \pm 3 \text{ eu}$ . The entropy of activation is quite negative, which is consistent with the dimerization of an anion leading to solvent organization due to charge localization.

NMR line for  $[\text{8}]^{2-}$  narrows over a period of several days.

In view of the evidence amassed for the decrease in the concentration of [8]annulene anion radical and the relatively slower increase in the concentration of the [16]annulene anion radical, Scheme I appears to fit all of the data. All of the reactions in Scheme I have been shown to take place independently either in this work or in previous reports. Reactions 7–10 have all been separately demonstrated to take place.<sup>6–10</sup>

#### Scheme I



Other than our preliminary communication, this represents the first report of the direct dimerization of anion radical.<sup>13</sup> The reaction does not appear to be of synthetic value because of the relatively rapid formation of polymeric material. However, this dimerization should prove to be a facile source of substituted [16]annulene anion radicals for ESR study, as the synthesis of substituted [16]annulenes is most laborious and only a couple are known.

#### Experimental Section

The concentration of the anion radical of [8]annulene was measured by comparing the doubly integrated ESR spectrum of  $[\text{8}]^{\cdot-}$  with that of a known concentration of DPPH. The samples were compared by utilizing a dual-cavity IBM Bruker ESR spectrometer. The overmodulated (modulation amplitude = 25 G) ESR data for both sample and standard were sent directly to a MINC II computer system where the double integrations were carried out. The magnitudes of the double integrations are directly proportional to the anion radical concentrations. Thus by comparing these double integrations to those taken from the DPPH spin standard, we were able to obtain the total anion radical ( $[\text{8}]^{\cdot-} + [\text{16}]^{\cdot-}$ ) concentration in a given sample. The ratio of the concentrations of  $[\text{8}]^{\cdot-}$  and  $[\text{16}]^{\cdot-}$  was obtained from the computer simulations of spectra that

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were recorded with a low modulation amplitude ( $5 \times 10^{-2}$  G). Knowing the total anion radical concentration and the ratio of the two concentrations gives us the concentration of both anion radical species. Sensitivity bias between the two cavities was corrected for by carrying out comparisons of doubly integrated spectra of identical DPPH samples in each of the cavities.

ESR and/or NMR samples were sealed from the all-glass apparatus under high vacuum. Weighed portions of the salts were placed directly in the ESR or NMR tubes prior to initiation of the experiment. In this way, the salts could be kept under high vacuum for several hours prior to the addition of the solvent. This technique also allowed us to take ESR and NMR samples of the same solution with no salt present and with

various concentrations of the salt added. The concentrations of added KI and NaI varied from 0.01 to 0.1 M.

Neutral [8]annulene was added to the anion radical solutions via break seals. The amount of metal used in the reduction was varied so as to keep the anion radical concentration constant.

NMR spectra were recorded on a Perkin-Elmer 60-MHz spectrometer. The HMPA was purified as previously described<sup>12</sup> and was distilled directly into the apparatus where the reductions were carried out. All of the reductions took place on a freshly distilled sodium surface under high vacuum.

Registry No. [8]<sup>-</sup>, 34510-85-5.

## Energetics and Hydration Structures of a Solvated Gramicidin A Transmembrane Channel for K<sup>+</sup> and Na<sup>+</sup> Cations

Kwang S. Kim and E. Clementi\*

Contribution from IBM Corporation, Department 48B, Kingston, New York 12401.

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**Abstract:** This paper analyzes the strength of the interaction energies of the K<sup>+</sup> and Na<sup>+</sup> ions with GA along a transmembrane channel axis. The detailed hydration structures in the channel in the presence of these ions are described from Monte Carlo simulations. The nine water molecules inside the channel strongly hydrate the GA carbonyl oxygens. The interaction energy of these water molecules with GA is much larger than that with water or an ion. This fact, combined with the small cross sections of the GA channel, suggests that an ion will push a column of water ahead of it in order to pass through the channel. The energetics of solvation and hydration are also analyzed. For a linear strand of water molecules in the channel, the contribution of the solvation energy from higher solvation shells decreases rapidly because we included bulklike water outside the channel mouth. Within a rigid GA frame, this work also indicates that inside the channel the Na<sup>+</sup> ion moves along a helical path in between two layers of GA backbone atoms, while the K<sup>+</sup> ion moves roughly linearly along the cylindrical axis of the channel.

### I. Introduction

The ion selectivity of a biological membrane plays an important role in many biomechanisms. At present, the gramicidin channel is the only ion-selective transmembrane with a well-characterized structure. This single transmembrane structure is impermeable to anions and divalent cations. However, it exhibits selectivity among monovalent cations with permeability ratios (with respect to sodium) of H<sup>+</sup>(150) > NH<sub>4</sub><sup>+</sup>(8.9) > Cs<sup>+</sup>(5.8) > Rb<sup>+</sup>(5.5) > K<sup>+</sup>(3.9) > Na<sup>+</sup>(1.0) > Li<sup>+</sup>(0.33), as earlier reported by Myers and Haydon.<sup>1</sup> Interest in the gramicidin channel has been enhanced due to its complex conductance properties, such as ion selectivity, voltage and concentration dependence of permeability ratios, etc., as the number and scope of studies has increased greatly in recent years. For recent reviews, see Urry,<sup>2</sup> Ovchinnikov,<sup>3</sup> Eisenman and Horn,<sup>4</sup> and Andersen.<sup>5</sup>

Since GA has a relatively simple and well-defined structure, there is a wealth of experimental data. Many conformational studies,<sup>6</sup> simple electrostatic model studies,<sup>7</sup> and simple molecular

dynamics (MD) studies<sup>8</sup> have also been reported. Although some of these reports show reasonable agreement with experiment, some of the models used are still too simple to be reliable, or the reliability of some potentials used is questionable.

Wilson et al.<sup>9</sup> recently studied the interaction of GA with cations and a few water molecules by using MD techniques. Although their model included intramolecular interaction energies of GA, it still used vacuum instead of bulk water outside the channel; thus, energy profiles cannot be easily obtained owing to the neglect of solvation effects by bulk water and the temperature fluctuations in MD techniques (which are caused by the small number of water molecules and one cation). In particular, as noted in their paper, uncertainties in the potentials used were one of the shortcomings of the study. Other recent theoretical studies of energy profiles of Na<sup>+</sup> interacting with GA have been reported by Pullman et al.<sup>10</sup> In their papers, however, solvation effects and temperature and statistical effects were not considered. Furthermore, the binding energy of Na<sup>+</sup> and GA was obtained by using parameters which were fitted to mimic the results of ab initio calculations on small systems.

To lessen potential problems, we recently reported the ab initio atom-atom pair interaction energies of potassium,<sup>11</sup> sodium,<sup>12</sup> and

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