Liberation of Hydrogen from an Anion Radical Pyrolysis

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The thermodynamically stable solid polyacene anion radical–alkaline earth metal–ammonia complexes [$M^{2+}(NH_3)_2(P^-\cdot)_2$] liberate hydrogen gas and ammonia when heated to temperatures above 100 °C. Simultaneous with the liberation of these two gases, the polyacene itself undergoes a polymerization reaction. It has been found that the hydrogen produced originates, for the most part, from the polyacene as opposed to the ammonia. It is the loss of H_2 that allows the polymerization of the polyacene. The simple degradation of the complex back to the metal, ammonia, and polyacene is favored by the smaller polyacenes, while the polymerization coupled with the hydrogen production is favored by the larger systems.

Polyaromatic anion radical salts are both kinetically and thermodynamically stable.[1,2] Just like their neutral analogues, both the solid salts and tetrahydrofuran (THF) solutions of the anion radicals of polyacenes (P), for example, tetracene (TE), anthracene (AN), pyrene (PY), naphthalene (NP), and perylene (PE), persist for years at temperatures up to 100 °C. However, a number of more complex anion radicals do undergo some interesting thermally induced transformations. For example, the tetrahydrofuran (THF) solvated anion radical of *cis*-stilbene spontaneously rearranges to the trans isomer,[3] the anion radicals of (*p*-nitrophenyl)methyl halides lose the halide anion[4] upon warming, and both the [8]annulene[5] anion radical and the parasubstituted benzaldehyde[6] anion radicals dimerize to initially form dianions. Despite the variety of thermal anion radical rearrangements and decompositions that have been observed, none have been reported for the polyacene anion radical systems. Here we report a new and novel thermal decomposition process for the solid polyacene anion radicals that results in the liberation of hydrogen gas.

The solid alkali metal–anion radical salts of all of the polyacenes mentioned above [$M^+_2\,(P^-\cdot)_2$] can be generated via sodium reduction of the neutral molecules and a simple distillation of the solvent from the salt under high vacuum.[1,2,7] In liquid ammonia, barium, strontium, or calcium metal will reduce these polyacenes to their anion radicals. However, removal of the solvent (NH_3) leaves anion radical–ammonia complexes [$M^{2+}(NH_3)_2(P^-\cdot)_2$], which are thermochemically stable and have heats of generation from the metal, polyacene, and ammonia in their standard states that vary from -40 to -78 kcal/mol, reaction 1.[1,2]

$$M(s) + 2NH_3(g) + 2P(s) \rightarrow M^{2+}(NH_3)_2(P^-\cdot)_2(s) \quad (1)$$
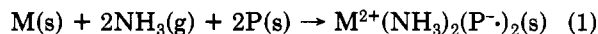
$$\text{for P = AN} \quad \Delta H° = -40 \text{ kcal/mol}$$

$$P = PY \quad \Delta H° = -50 \text{ kcal/mol}$$

Here we report that warming these stable solid salts to temperatures of less than 150 °C generates appreciable quantities of hydrogen gas, with subsequent polymerization of the polyaromatic. This is a most surprising reaction in

view of the fact that both the polymerization and dehydrogenation of polyaromatics are extremely difficult. Yet simple heating of these systems with an added electron results in these two processes.

Results and Discussion

When solid samples of $M^{2+}(NH_3)_2(P^-\cdot)_2$ are heated to 140–150 °C in a closed vacuum system that is fitted with a capacitron for monitoring the pressure, hydrogen gas is liberated, Figure 1. From Figure 1 it is clear that when P = pyrene close to 0.1 mol of hydrogen gas per mol of salt radical can be generated in a 24 h period. When anthracene⁻· serves as the anion radical, only about 0.02 mol of H_2 per mol of salt can be generated at 100 °C. The much smaller yield of hydrogen gas from the anthracene systems (the naphthalene salt yields even smaller amounts of H_2) results, in part, from the fact that the complex simultaneously degrades back to its constituents while liberating the hydrogen gas, reaction 2.

$$Ba^{2+}(NH_3)_2(NP^-\cdot)_2 \rightarrow H_2 + polymer$$

$$Ba^{2+}(NH_3)_2(NP^-\cdot)_2 \rightarrow Ba + 2NP + 2NH_3 \quad (2)$$
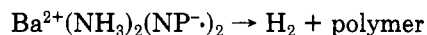
For the salt described in reaction 2, 1.26 mol of ammonia and 1.4 mol of naphthalene per mol of salt are recovered from the pyrolysis. The remainder of the hydrocarbon, metal, and ammonia are found in a black intractable solid, which has the appearance of anthracite coal. This solid polymeric material proves to be 71% carbon, 12.9% oxygen (actual analysis), 1.4% nitrogen, and 4.6% hydrogen upon elemental analysis. The presence of the oxygen is due to the workup of the material after pyrolysis. This workup consisted of exposure to air and washing with water and acetone. The presence of the nitrogen in the black solid is clearly due to the incorporation of ammonia in the polymer.

Similar results were realized for the pyrolysis of the barium–ammonia–anthracene complex ($M^{2+} = Ba^{2+}$ and P = AN). Surprisingly, measurable amounts of hydrogen gas were liberated at temperatures as low as 60 °C. As can be seen from Figure 1, increasing the temperature greatly increases the hydrogen production. When this same anthracene complex is heated to 166 °C, 0.74 mol of NH_3 and 0.12 mol of H_2 per mol of salt are liberated during the first 24 h of pyrolysis. It should be kept in mind that the salt could theoretically yield 2 mol of ammonia/mol of salt. Again heating the remaining black solid that has never been exposed to air to bunsen burner temperatures liberates considerably more hydrogen and ammonia. In fact more than 2.5 mol of hydrogen and 1.7 mol of ammonia/mol of salt can be realized from these high-temperature pyrolyses.

(1) Stevenson, G. R.; Schock, L. E.; Concepcion, R.; Peterson R. *J. Phys. Chem.* **1985**, *89*, 175.
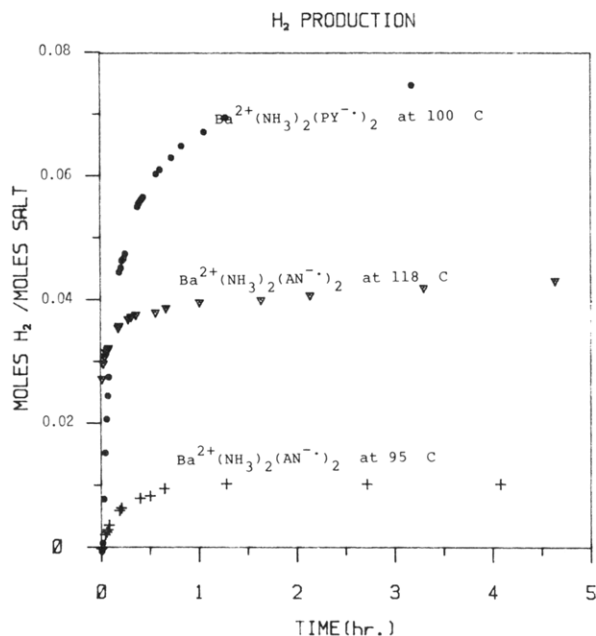(2) Stevenson, G. R.; Schock, L. E. *J. Am. Chem. Soc.* **1983**, *105*, 3742.
(3) Wang, H. C.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1977**, *99*, 2642.
(4) Neta, P.; Behav, D. *J. Am. Chem. Soc.* **1980**, *102*, 4798.
(5) Stevenson, G. R.; Reiter, R. C.; Sedgwick, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 6521.
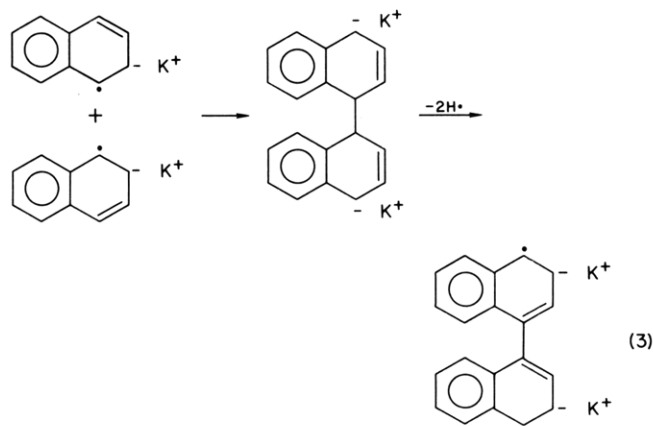(6) Armstrong, N. R.; Quinn, R. K.; Vanderborgh, N. E. *J. Phys. Chem.* **1977**, *81*, 657.
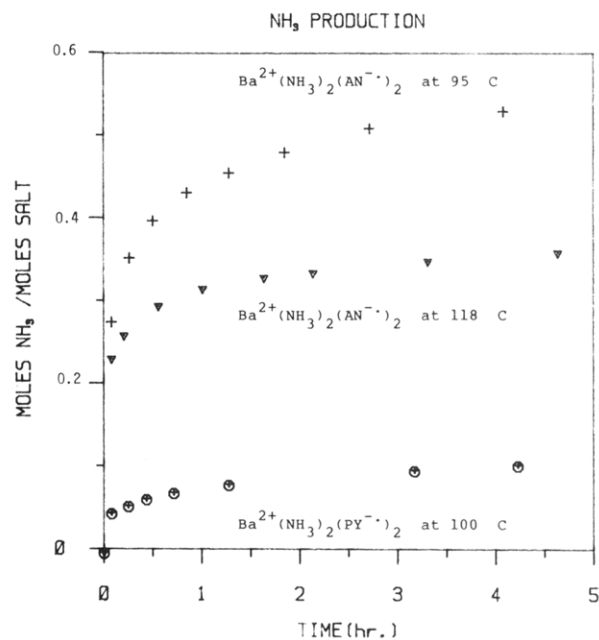(7) Stevenson, G. R.; Peterson, R. *J. Org. Chem.* **1984**, *49*, 3443.

Figure 1. Plots of moles of hydrogen produced per mole of salt used in the pyrolysis vs. time. The salts and the pyrolysis temperatures are given next to the curves.

Figure 2. Plots of moles of ammonia liberated per mole of salt used in the pyrolysis vs. time. The salts and the pyrolysis temperatures are given next to the curves.

Even more and faster liberation of ammonia takes place when the larger polyaromatics serve as the polyacene. An example of this is shown in Figure 1, where pyrene serves as the polyacene. The polymerization of the anion radical salt must be initiated by the simple dimerization of the anion radical, reaction 3. The resulting dianion is sta-

bilized by the presence of the barium cation. The loss of hydrogen then leaves a bipolyacene dianion, which can then dimerize or combine with another anion radical to perpetuate the process. If this mechanism is correct, the presence of nitrogen in the polymer must be due to physically trapped ammonia. This is substantiated by the fact that more ammonia can be liberated by simply reheating the black solid with a bunsen burner. The mechanism proposed in reaction 3 also suggests that the hydrogen that is liberated upon pyrolysis originates from the hydrocarbon and not the ammonia. The fact that more than 1 mol of hydrogen/mol of P can be generated means that there must be considerable branching during the polymerization. It is clear from Figure 1 that the production of hydrogen at a given pyrolysis temperature ceases after about 5 or 6 h. This must be due to the fact that the degree of crosslinking of the polymer strands is controlled by the reaction temperature and is a fixed value for each salt at a given temperature. Increasing the temperature of a sample that has terminated its hydrogen

production results in further evolution of H_2.

Simultaneously with the production of H_2 is the liberation of ammonia from the complexes, Figure 2. For all of the complexes studied more ammonia is liberated than hydrogen produced. However, increasing the size of the polyacene actually decreases the rate of ammonia production. This is opposite to the effect upon H_2 production. Increasing the size of the aromatic increases the thermodynamic stability of the anion radical via the increase in the electron affinity of the neutral molecule. This renders the anion radical less prone to "spit" the electron back into the metal and consequently free the ammonia. Once the electron is given back to the metal the polyacene is freed, as is the ammonia, and it sublimes from the apparatus. This of course also limits the production of hydrogen. This is consistent with the fact that free polyacene is, indeed, found in the first U-tube. From Figures 1 and 2, it is clear that both the generation of hydrogen and of free ammonia cease simultaneously. This is consistent with the trapping (either physical or in the form of a metal ammonia complex) of the ammonia in the polymer complex.

Samples of the barium–naphthalene salt were generated by using perdeuterated naphthalene to check if this is the case. The pyrolysis of these deuterated salts yield a mixture of D_2, HD, and H_2. This mixture proved to consist of 29% deuterium and 71% H atoms. The presence of ^{1}H clearly means that some of the hydrogen, at least, originated from the ammonia. However, the possibility exists that the protons on ammonia and those on the naphthalene anion radical exchange prior to the crystallization of the solid complex, reaction 4. To check upon this pos-

$$C_{10}D_8^{-} \cdot + NH_3 \rightarrow NH_2D + C_{10}D_7H^{-} \cdot \quad (4)$$

sibility, we generated the anion radical of naphthalene-d_6 in ammonia. Within 20 min after the reduction of the NP-d_6 with barium metal, the ESR spectrum of the ammonia solution indicated the presence of $C_{10}D_7H^{-} \cdot$. After a 24-h period, the anion radical of naphthalene ($C_{10}H_8^{-} \cdot$) could be observed from the ESR spectrum. Thus, the protons on ammonia and naphthalene anion radical undergo exchange. The studies with deuterated naphthalene prove that at least a major portion of the H_2 that is lib-

erated during the pyrolysis of $Ba^{2+}(NH_3)_2(NP^-\cdot)_2$ originates from the naphthalene. This is consistent with the mechanism proposed in reaction 3. However, the deuteration studies do not eliminate the possibility that the H_2 comes from the ammonia in the final step. The fact that the amount of hydrogen produced varies dramatically with the choice of hydrocarbon supports the mechanism proposed in reaction 3.

It appears that significant amounts of hydrogen can be generated regardless of the polyacene used. Studies carried out with calcium and strontium serving as the metal yield very similar results. In fact, the yield of hydrogen from the $Ca^{2+}(NH_3)_2(AN^-\cdot)_2$ salt was indistinguishable from that of the analogous barium salt.

Experimental Section

The alkaline earth metal complexes were generated via the reduction of the polyaromatic hydrocarbons with 1 equiv of the alkaline earth metal in liquid ammonia in a manner that is identical with that previously described.[1] The pyrolysis studies were carried out by heating evacuated bulbs containing the solid salts in an oil bath. The evacuated bulbs were connected to a vacuum line through two U-tubes. The U-tube closest to the bulb containing the salt was kept under a dry ice–acetone bath at –78 °C, and the second U-tube was immersed in liquid nitrogen. After the vacuum line was pumped down to about 10^{-6} mmHg, a breakseal separating the bulb and the U-tubes and vacuum system was broken. The pressure in the vacuum system was monitored with a Fluid Precision Inc. capacitron pressure gauge to ±0.01 mm of Hg. From the known volume of the vacuum system, the number of mol of gas that passed through the two U-tubes was obtained. When these noncondensable gases were exposed to hot copper oxide, the pressure dropped to zero and a mole of water was condensed from the vacuum line for each mole of gas present. This coupled with the NMR analysis of liquid formed from the reaction of the gas with CuO confirms the fact that the gas was uncontaminated hydrogen.

The number of moles of liquid N_2 condensable gases emitted from the pyrolyzed salt was obtained by pumping the noncondensables from the system and then removing the liquid nitrogen bath from the second U-tube. Unpolymerized hydrocarbon was recovered from the U-tube immersed in the dry ice–acetone bath.

Mass spectral analyses were carried out with a HP 5790 mass selective detector, and the analytical samples were sent to Micro-Analysis, Inc. for elemental analyses. ESR spectra were recorded with a Bruker (IBM) E-2000 ESR spectrometer.

Conclusions

It has been found that heating solid samples of the alkaline earth metal–ammonia–polyaromatic anion radical complexes to temperatures above 60 °C yields significant amounts of hydrogen gas. This hydrogen gas appears to originate from the aromatic hydrocarbon anion radical and results in the subsequent polymerization of the polyaromatic. Simultaneously with this reaction, there is some degradation of the complex back to the metal, ammonia, and polyacene. This simple decomposition is favored by small polyacenes (those with low electron affinities), while the production of hydrogen is favored by the larger polyacene systems.

Thermolysis of Highly Congested Tri-*tert*-alkylmethanols: Strain Energies of Bridgehead Alkyl Radicals

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The rate constants and the products of the thermolysis of tertiary alcohols, $R^1R^2R^3COH$, where R^i is *tert*-butyl, 1-adamantyl, 1-bicyclo[2.2.2]octyl, or 1-norbornyl, have been determined. Apart from the usual secondary alcohols and ketones, the products include new ketones, formed by ring-opening of the 1-norbornyl group, and solvent-incorporated alcohols. The activation energies for (*t*-Bu)–C, Ad–C, Oc–C, and, in one case, Nor–C cleavage are compared with the molecular mechanics calculated strain-energy changes, Δstrain. These latter are based on a simple model of the reaction intermediate where the bridgehead radicals are represented by the corresponding alkanes. Taking the $\Delta G^{\ddagger}$(200 °C)/Δstrain correlation for *t*-Bu· formation as a reference, one can show that the deviations, $\Delta\Delta$strain, of the data for the formation of the other radicals (Ad, 2.4; Oc, 4.0; Nor, 7.7 kcal mol^{-1}) indicate the real difference between the strain energies of the radicals and the alkanes. Analogous $\Delta\Delta G^{\ddagger}$ data for other reactions considered to involve rate-determining radical formation correlate with $\Delta\Delta$strain, the slopes ranging from 0.16 to 1.13. The $\Delta\Delta$strain values also correlate with solvolysis rate constants of *tert*-alkyl tosylates, with a slope ($\Delta\Delta$strain/$\Delta G^{\ddagger}$(70 °C)) of 0.36; tentative values for the strain energies of other bridgehead radicals are proposed and compared with the predictions of a radical force field.

It is generally agreed that tertiary alkyl radicals accept nonplanarity more easily than tertiary alkyl cations.[1] According to the latest calculations and interpretation of ESR spectra,[2] even the *tert*-butyl radical is slightly non-planar. The result of this difference between radicals and carbocations is that solvolysis rates of bridgehead alkyl derivatives[3] range over many powers of 10, from 1-adamantyl (1) to 1-norbornyl (10^{-10}), for example, while the relative rates of reactions with rate-determining formation of the corresponding radicals differ much less (Ad/Nor = $10^{0.6}$–10^4).[4] However, the several studies re-

(1) (a) Fort, R. C.; Schleyer, P. v. R. *Adv. Alicycl. Chem.* **1966**, *1*, 284. (b) Fort, R. C. "Adamantane—The Chemistry of Diamond Molecules"; Dekker: New York, 1976; pp 233–265.

(2) (a) Paddon-Row, M. M.; Houk, K. . *J. Am. Chem. Soc.* **1981**, *103*, 5046. (b) Griller, D.; Ingold, K. U.; Krusic, P. J.; Fischer, H. *Ibid.* **1978**, *100*, 6750.

(3) Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189.