UV-vis spectroscopy is not sufficient to characterize the highly colored, soluble intermediates in the pyrolysis of **1**, particularly since any sort of "quantum confinement" (one-, two-, or three-dimensional) would lead to the observed changes in absorption. Transmission electron microscopy provides more definite structural assignment since it allows the imaging of distinct particles. The micrograph shown in Figure 3 indicates that the soluble intermediates in the pyrolysis of Cd(SePh)$_2$ are nanoclusters of CdSe. The electron diffraction pattern of this material is consistent with that of CdSe. These clusters are structurally similar to those previously prepared by arrested precipitation and organic capping,[7f] although chemically they are different in being slightly air sensitive.

In this report we have shown that nanoscale compounds can be prepared by the solution phase thermolysis of molecular precursor compounds. This technique is a valuable complement to the now familiar arrested precipitation and offers the chance to prepare nanoclusters of materials which cannot easily be formed by simple precipitation. This work also directly demonstrates the intermediacy of large clusters in the formation of solid-state compounds by the precursor method.

Supplementary Material Available: Tables listing positional and thermal parameters, significant distances and angles, and X-ray powder patterns of the products of the thermolysis reactions and an electron diffraction pattern of the TEM sample (15 pages); table of calculated and observed structure factors (34 pages). Ordering information is given on any current masthead page.

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(10) All reactions were done under inert atmosphere using dry, degassed solvents. To Me$_2$Cd (Alfa, 0.15 g, 11 mmol) in toluene (10 mL) was added HSePh (Aldrich 0.34 g, 22 mmol) in toluene (5 mL). A white solid formed immediately. The reaction mixture was stirred for 4 h, and the white precipitate was collected, washed repeatedly with heptane, and dried in vacuo to give a white solid (0.38 g, 80%): mp >304 °C; ^{1}H NMR (pyr-d_5, 30 °C) 8.03 (2 H), 7.00 (3 H); visible spectrum (HP-8451A) λ_{max} = 315 nm. Anal. Calcd for C$_{12}$H$_{10}$CdSe$_2$: C, 34.2; H, 2.37. Found (Schwarzkopf): C, 34.6; H, 2.54.

(11) To a solution of Me$_2$Cd (0.15 g, 11 mmol) and Et$_2$PCH$_2$CH$_2$PEt$_2$ (Strem, 0.18 g, 9 mmol) in toluene (10 mL) was added HSePh (0.34 g, 22 mmol) in a dropwise fashion. After a period of minutes to hours, a white precipitate formed (0.45 g, mp 162–3 °C). Recrystallization from pyridine-/heptane (1:8) gave colorless needles (0 17 g, 28%): mp 158.6–159 °C; ^{1}H NMR (pyr-d_5, 30 °C) 8.06 (4 H), 7.04 (6 H), 1.67 (2 H), 1.46 (4 H), 1.02 (6 H). Anal. Calcd for C$_{17}$H$_{22}$CdPSe$_2$: C, 38.6; H, 4.49; P, 5.85. Found: C, 38.9, H, 4.27; P, 5.88.

(12) Refinement procedures were as described elsewhere.[13] The complex crystallizes in the monoclinic space group $P2_1/c$ with a = 21.867 (8) Å, b = 22.261 (8) Å, c = 8.131 (2) Å, β = 100.08 (5)°, V = 3896.92 Å^3, Z = 8, d(calcd) = 1.733 g/cm^3, and μ (Mo Kα) = 4.89 mm^{-1}. A CAD4 diffractometer was used to collect 8429 reflections (5092 unique) in the range 5 < 2θ < 45° at 28 °C. Data (3785) with $I_{net} > 2.5\sigma(I_{net})$ were used in refinement. Refinement of 380 parameters gave residuals of R_f = 0.091 and R_w = 0.075. The goodness of fit index was 7.659, and the largest shift/esd = 0.156.

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(15) Both compounds were sealed in Pyrex under vacuum. Compound **1** (95 mg) was brought initially to 400 °C and then held at 350 °C for 24 h to give CdSe (40 mg, 97%). Compound **2** (72 mg) was brought to 350 °C and then held at 320 °C for 24 h to give CdSe (24 mg, 90%). X-ray powder patterns (Rigaku Miniflex, λ = 1.5418 Å) of both reaction products are included in the Supplementary Material.

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Determination of Homolysis Energies in Solution from Heterolysis Enthalpies and Electron-Transfer Energies

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Received March 2, 1989

During the past 5 years we have developed a method for determining heats of heterolysis (ΔH_{het}) from the calorimetric heats of reaction ($\Delta H_{het} = -\Delta H_{reaction}$) of carbocations with carbanions, phenoxide, imide, and thiolate anions in solution.[1] Well over 100 values have been determined by this method for C–C, C–O, C–N, and C–S bonds from resonance-stabilized precursors and the ΔH_{het}'s are related in a remarkably simple manner to the pK_{R^+} of the carbocation and the pK_a of the conjugate acid of the anion.[1-3]

We now show that by combining the ΔH_{het}'s with the redox potentials of the cations and anions through a simple thermodynamic cycle, heats of homolysis (ΔH_{homo}) may be calculated, and the complete set of energetics for homolytic, heterolytic, and electron-transfer reactions related to each other. These data provide the first available quantitative criteria for the selective cleavage of such bonds in macromolecules to give resonance-stabilized cations, anions or radicals. Our method is closely analogous to Bordwell's approach[4,5] for the determination of bond dissociation energies for C–H bonds (BDE$_{C-H}$) but differs in that a variety of carbocations take the place of the proton.

Scheme I combines the redox potentials of the separate cationic and anionic species with the heats of heterolysis referred to above. The difference between the heterolysis and homolysis energies is the Gibbs free energy of electron trnasfer, ΔG_{ET}, obtained from the redox potentials of the cation and anion.

Two obstacles might stand in the way of applying this approach. First is the difficulty of obtaining reversible redox potentials for the carbocations and carbanions using ordinary cyclic voltammetry (CV). We have applied second harmonic AC voltammetry (SHACV)[6] to successfully determine reversible potentials which confirm Bordwell's irreversible CV values for a number of anions.

The second problem is more fundamental—the mingling of ΔH_{het} enthalpic measurements with redox free energy terms. Application of Scheme I requires that the entropy terms associated with electron transfer will have a negligible effect on combining the ΔG_{ET} terms with ΔH_{het}. If $\Delta S_{ET} = 0$, then $\Delta G_{ET} = \Delta H_{ET}$. Various arguments and several published reports[4,7,8] support this assumption, but a more compelling argument is our demonstration that the temperature coefficients of the redox potentials, $-(\partial \Delta G_{redox}/\partial T) = \Delta S_{redox}$ are small for relevant ions.

Table I presents data for trityl and triphenylcyclopropenium cations which represent the extremes of the stability range of ten carbocations that we have studied with a variety of anion types. The family of substituted fluorenide anions shown here duplicates, for the most part, the studies by Bordwell's group.[4,5,9] Stein's estimate[10] of less than 15 kcal/mol for the trityl–trityl bond in hexaphenylethane corresponds well with our determined value of 13 ± 3.5 kcal/mol for ΔH_{homo} for the trityl–9-phenylfluorenyl bond.

Several trends and correlations are noteworthy that are established with the full data set which is presently being prepared for publication. Properties which involve the conversion of a neutral species to an ion or vice versa (e.g., pK_a, pK_{R^+}, ΔH_{het}, ΔG_{ET}, and redox potentials) all correlate quite well with each other.[1-3] The overwhelming factor in such cases is the distribution of charge

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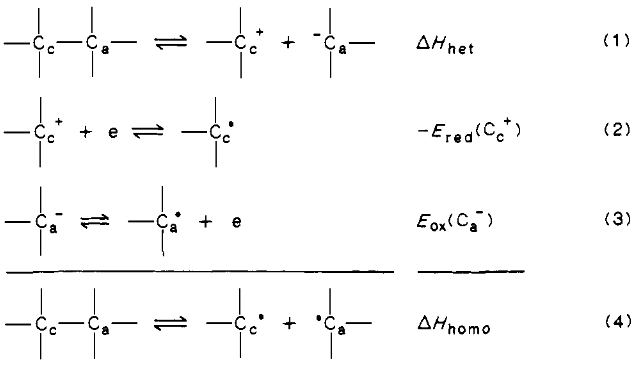
Table I. Heats of Heterolysis, Homolysis, and Free Energy of Electron Transfer (kcal/mol) of Two Carbocations with Fluorenyl Anions in Sulfolane/3-Methylsulfolane (5%) at 25 °C

			cation					
			trityl pK_{R^+} = −6.63 $E_{1/2}$(red) = −0.133 V			triphenylcyclopropenylium pK_{R^+} = 3.1 $E_{1/2}$(red) = −1.304 V		
anions	pK_a	$E_{1/2}$(ox),[a] V	ΔH_{Het}[b]	ΔG_{ET}	ΔH_{Homo}[c]	ΔH_{Het}[b]	ΔG_{ET}	ΔH_{Homo}[c]
9-PhFl	17.9	−1.101 (−1.028)	35.51 ± 0.56	−22.32	13.18	29.34 ± 0.28	4.68	34.02
9-PhSFl	15.4	−0.882 (−0.849)	33.61 ± 0.34	−17.27	16.34	27.49 ± 0.18	9.73	37.22
2-Br-9-PhSFl	13.2	−0.732 (−0.720)	29.41 ± 0.52	−13.81	15.60	25.40 ± 0.50	13.19	38.59
9-PhSO$_2$-Fl	11.55	−0.392 (−0.309)	28.35 ± 0.59	−5.97	22.38	22.23 ± 0.36	21.03	43.26
9-CO$_2$Me-Fl	10.35	−0.555 (−0.492)	25.81 ± 0.42	−9.73	16.08	20.62 ± 0.12	17.27	37.89
9-CN-Fl	8.30	−0.481 (−0.424)	24.62 ± 0.62	−8.02	16.60	19.56 ± 0.30	18.98	38.54
2,7-Br$_2$-9-CO$_2$Me-Fl	6.52	−0.286 (−0.243)	19.76 ± 0.85	−3.53	16.23	16.22 ± 0.10	23.48	39.70

[a] Reversible $E_{1/2}$ of oxidation from anion to radical vs the $E_{1/2}$ of ferrocene/ferrocenium measured in sulfolane/3-methylsulfolane at 25 °C by cyclic voltammetry or second harmonic AC voltammetry on a BAS-100A Electrochemical Analyzer. Standard deviation = ±15 mV. Parentheses contain irreversible E_{ox} in DMSO measured by CV in Bordwell's laboratories.[9] [b] ΔH_{Het} measured in a calorimeter at 25 °C using $\Delta H_{Het} = -\Delta H_{Rxn}$. [c] Calculated by using the equation, $\Delta H_{Homo} = \Delta H_{Het} + \Delta G_{ET}$ where $\Delta G_{ET} = 23.06[E_{1/2}(C^-) - E_{1/2}(C^+)]$; standard deviation = ±3.5 kcal/mol.

Scheme I



$$-C_c-C_a- \rightleftharpoons -C_c^{+} + {}^{-}C_a- \qquad \Delta H_{het} \qquad (1)$$

$$-C_c^{+} + e \rightleftharpoons -C_c^{\bullet} \qquad -E_{red}(C_c^{+}) \qquad (2)$$

$$-C_a^{-} \rightleftharpoons -C_a^{\bullet} + e \qquad E_{ox}(C_a^{-}) \qquad (3)$$

$$-C_c-C_a- \rightleftharpoons -C_c^{\bullet} + {}^{\bullet}C_a- \qquad \Delta H_{homo} \qquad (4)$$

$$\Delta H_{homo} = \Delta H_{het} - E_{red}(C_c^{+}) + E_{ox}(C_a^{-}) \qquad (5)$$

internally by resonance or externally by solvation. On the other hand ΔH_{homo}'s and BDE$_{C-H}$'s involve the creation of uncharged radicals from neutral molecules. These properties are much less sensitive to structural variation than the five listed above, and they do not correlate with them, although ΔH_{homo} and BDE's (not shown) do correlate with each other. Significantly, a plot of ΔH_{het} vs ΔH_{homo} is a random scatter of points.

The method reported here offers the first opportunity to obtain quantitative comparisons between homolytic and heterolytic bond energies over a wide range of structure variation from experimental data in solution.

Acknowledgment. This work was made possible by Grant No. 5088-260-1643 from the Gas Research Institute for which we are most grateful.

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Additions and Corrections

Reversible Metal–Metal Bond Cleavage Accompanied by the Facile Reversible Addition of H_2 to a Ru_3 Cluster. Synthesis and X-ray Structures of $Ru_3(CO)_8(\mu\text{-}H)_2(\mu\text{-}t\text{-}Bu_2P)_2$ and $Ru_3(CO)_8(\mu\text{-}H)_2(H)_2(\mu\text{-}t\text{-}Bu_2P)_2$ [*J. Am. Chem. Soc.* **1988**, *110*, 6894–6895]. ATTA M. ARIF, THERESA A. BRIGHT, RICHARD A. JONES,* and CHRISTINE M. NUNN

Page 6894: Reference 2 should include the following. For the facile activation of hydrogen by unsaturated Os_4 clusters see: Adams, R. D.; Wang, S. *Organometallics* **1986**, *5*, 1272. Adams, R. D.; Wang, S. *Inorg. Chem.* **1986**, *25*, 2534.

Page 6895: The acknowledgment section should also include the following sentence. We thank Professor R. D. Adams, University of South Carolina, for helpful discussions.