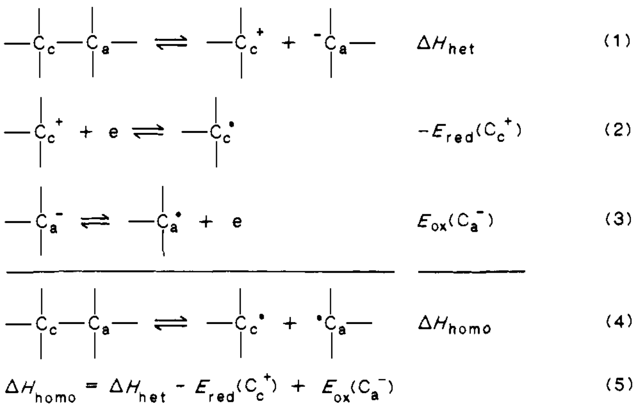
Table I. Heats of Heterolysis, Homolysis, and Free Energy of Electron Transfer (kcal/mol) of Two Carbocations with Fluorenyl Anions in Sulfolane/3-Methylsulfolane (5%) at 25 °C

			cation					
			trityl $pK_{R^+} = -6.63$ $E_{1/2}(\text{red}) = -0.133$ V			triphenylcyclopropenylium $pK_{R^+} = 3.1$ $E_{1/2}(\text{red}) = -1.304$ V		
anions	pK_a	$E_{1/2}(\text{ox})$,[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_2Me-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_2Me-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 $\Delta H_{\text{Het}} = -\Delta H_{\text{Rxn}}$. [c] Calculated by using the equation, $\Delta H_{\text{Homo}} = \Delta H_{\text{Het}} + \Delta G_{\text{ET}}$ where $\Delta G_{\text{ET}} = 23.06[E_{1/2}(C^-) - E_{1/2}(C^+)]$; 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.

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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.