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Enthalpies of Cleavage for a Series of Radical Cations and Radical Anions: Comparison with Heats of Homolysis and Heterolysis of Their Neutral Precursors

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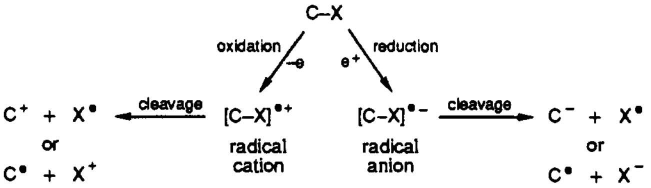
Abstract: Enthalpies of cleavage (ΔH_{cleav}) of the derived radical ions were determined at 25 °C in 95% sulfolane/5% 3-methylsulfolane by carrying out electrochemical oxidation and reduction of neutral molecules prepared by the reactions of a series of 9-substituted fluorenyl anion salts with four resonance-stabilized carbenium ion salts. Correlations are attempted between these results and other previously determined thermodynamic properties. Excellent correlations were obtained between ΔH_{cleav} for both types of radical ions and the heats of homolysis of their neutral precursors. Only scatter diagrams resulted from plots of the ΔH_{cleav}s versus the corresponding heats of heterolysis for the same neutral precursors. This behavior follows a previously observed pattern that, for these compounds (and perhaps more generally), properties which involve the gain or loss of charge correlate with each other but not with properties involving no change in charge. ΔH_{cleav}s for radical cations are strongly exothermic, implying a low barrier for rupture of the sessile bond. In every case, the slope for ΔH_{cleav} of the radical cations versus ΔH_{homo} of their precursors was positive and less than unity while those of corresponding plots for the radical anions were negative and close to one. The results presented here provide an unprecedented comparison of bond cleavage energies for radical cations, radical anions, heats of homolysis and heterolysis of directly comparable neutral structures, and also redox properties of the component ions for which pK_a and pK_{R^+} values are well established. The acidities of the radical cations derived from fluorenes were also determined from their pK_as in DMSO, their oxidation potentials, and those of their conjugate bases, viz. fluorenide ions. Three different electrochemical methods, cyclic voltammetry (CV), second harmonic alternating current voltammetry (SHACV), and Osteryoung square wave voltammetry (OSWV), were used to determine the redox potentials of the radical ionic species. Despite the time scales and apparent degrees of reversibility of these techniques, there was excellent agreement among the redox potentials obtained by these different methods.

Introduction

The making and breaking of covalent bonds is the most fundamental of organic chemical processes. An obvious consequence of the Lewis–Langmuir electron pair theory is the dichotomy of bond rupture for neutral molecules into two fundamental types, homolysis and heterolysis, since an electron pair can only sever in two ways. Recently we have shown how heats of heterolysis (ΔH_{het}s) for a series of highly unsymmetrical molecules can be obtained by solution calorimetry from the heats of reaction, or coordination ($\Delta H_{react} = -\Delta H_{het} = \Delta H_{coord}$) of carbenium ions with a variety of anions whose salts are stable in sulfolane (tetramethylene sulfone) at 25 °C under an atmosphere of argon.[1] Furthermore, by using several voltammetric techniques to obtain redox potentials of the various ions, most of the 200 ΔH_{het}s could be converted into heats of homolysis (ΔH_{homo}) provided that the redox potentials were reversible and the redox entropies ΔS_{redox} were negligible or could be calculated from the temperature coefficients of the redox potentials.[2]

The present paper extends these studies to the determination of heats of cleavage (ΔH_{cleav})[3] for the series of radical cations and radical anions produced by the electrochemical oxidation and reduction of the same series of neutral compounds whose ΔH_{het}s and ΔH_{homo}s have already been determined.

Scheme I



Scheme I demonstrates the formal relationship between heterolysis of the neutral molecule C–X by two possible pathways, the oxidation or reduction of C–X and of its component ions, and the enthalpies of cleavage of the radical cation and radical anion of C–X.

(a) For cleavage of the radical cation to $C^+ + X^\bullet$

$$[C\text{–}X]^{\bullet+} + e^- \rightarrow C\text{–}X \qquad -E_{ox}[C\text{–}X]$$

$$C\text{–}X \rightarrow C^+ + X^- \qquad \Delta H_{het}[C\text{–}X]$$

$$X^- - e^- \rightarrow X^\bullet \qquad E_{ox}(X^-)$$

$$[C\text{–}X]^{\bullet+} \rightarrow C^+ + X^\bullet \qquad \Delta H_{cleav}[C\text{–}X]^{\bullet+}$$

Thus

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[3] (a) Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2628, 2637. (b) Maslak, P.; Asel, S. L. *J. Am. Chem. Soc.* **1988**, *110*, 8260. (c) Maslak, P.; Narvaez, J. N. *J. Chem. Soc., Chem. Commun.* **1989**, 138. (d) Maslak, P.; Chapman, W. H., Jr. *J. Chem. Soc., Chem. Commun.* **1989**, 1809. (e) Maslak, P.; Narvaez, J. N. *Angew. Chem.* **1990**, *29* (3), 283. (f) Maslak, P.; Chapman, W. H., Jr. *J. Org. Chem.* **1990**, *55*, 6334. (g) Maslak, P.; Narvaez, J. N.; Kula, J.; Malinski, D. S. *J. Org. Chem.* **1990**, *55*, 4550. (h) Maslak, P.; Augustine, M. P.; Burkey, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 5359. (i) Maslak, P.; Narvaez, J. N.; Parvez, M. *J. Org. Chem.* **1991**, *56*, 602. Maslak has coined a series of terms to describe specific modes of radical ion cleavage.

0002-7863/91/1513-6967$02.50/0

$$\Delta H_{\text{cleav}}[\text{C–X}]^{\bullet+} = \Delta H_{\text{het}}[\text{C–X}] + 23.06\{E_{\text{ox}}(\text{X}^-) - E_{\text{ox}}[\text{C–X}]\} \tag{1}$$

(b) For cleavage of the radical anion to $\text{C}^\bullet + \text{X}^-$

$$\begin{array}{ll} [\text{C–X}]^{\bullet-} - e^- \rightarrow \text{C–X} & +E_{\text{red}}[\text{C–X}] \\ \text{C–X} \rightarrow \text{C}^+ + \text{X}^- & \Delta H_{\text{het}}[\text{C–X}] \\ \text{C}^+ + e^- \rightarrow \text{C}^\bullet & -E_{\text{red}}(\text{C}^+) \\ [\text{C–X}]^{\bullet-} \rightarrow \text{C}^\bullet + \text{X}^- & \Delta H_{\text{cleav}}[\text{C–X}]^{\bullet-} \end{array}$$

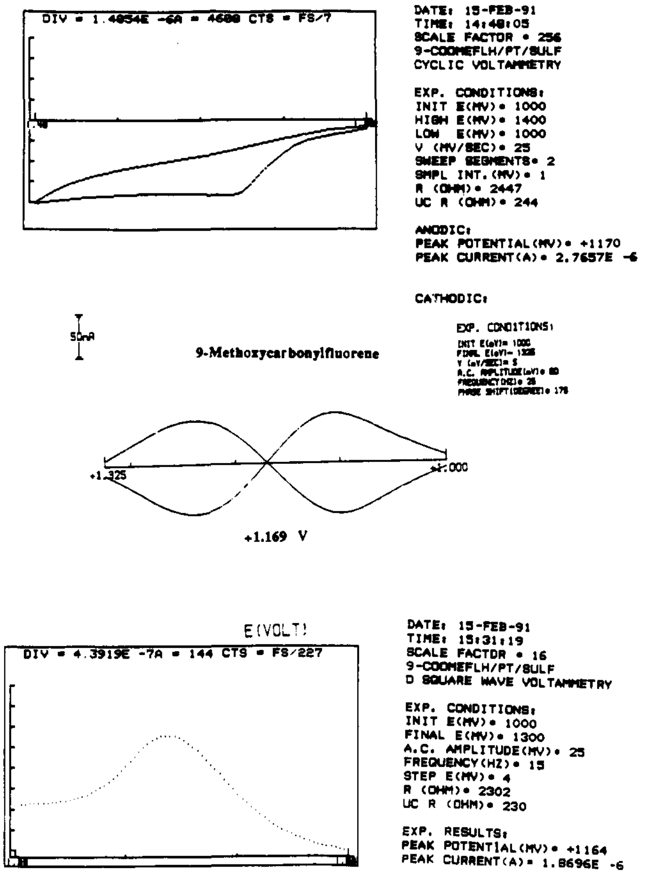
Thus

$$\Delta H_{\text{cleav}}[\text{C–X}]^{\bullet-} = \Delta H_{\text{het}}[\text{C–X}] + 23.06\{E_{\text{red}}[\text{C–X}] - E_{\text{red}}(\text{C}^+)\} \tag{2}$$

Since each of the compounds in this series of studies was prepared by the reaction of a resonance-stabilized carbenium ion with a stabilized anion of some sort (often a carbanion), only the heterolysis path to form C^+ and X^- is relevant to our actual experimental procedures. ΔH_{het} has been obtained from previous direct calorimetric measurements of heats of reaction of C^+ and X^-.[2] The approach in Scheme I is analogous to that employed by Bordwell for the determination of the pK_as of radical cations from the pK_as of Brönsted acids (fluorenes), their oxidation potentials, and those of their conjugate bases (fluorenide ions).[4] We have employed this method to obtain the acidities of the radical cations of the substituted fluorenes in Tables I–IV for comparison with the $\Delta H_{\text{cleav}}[\text{C–X}]^{\bullet+}$ of the corresponding carbon–carbon bonds.

As before,[1,2] we are limited to molecules whose precursor ions are sufficiently stable in sulfolane at 25 °C to allow preparation and handling during the calorimetric and electrochemical experiments. Of necessity, most are stabilized by resonance. Reversible redox potentials of the neutral molecules were required and usually obtained by cyclic voltammetry (CV),[5-8] second harmonic ac voltammetry (SHACV)[9,10] and Osteryoung square wave voltammetry (OSWV).[11-13] The merging of calorimetric enthalpy values with electrochemical free energy values must include ΔS_{redox} terms that were determined in several cases by temperature variation of the redox potentials although the resulting ΔS_{redox}s were usually negligible.

Results of the present study provide an unprecedented opportunity to compare the energetics for cleaving the same bond in a closely related series of molecules, radical cations, and radical anions for which many other types of data are available. Previous reports on radical ions have come from a variety of sources, most of which have been covered in a series of extensive and authoritative reviews.[14-21] The compounds and their radical ions have been chosen to be compatible with the techniques used to study them, and these cover a wide range of photochemical[16,22-24] and electrochemical techniques[16,25-27] as well as those based on



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EXP. CONDITIONS:
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HIGH E(MV)= 1400
LOW  E(MV)= 1000
V (MV/SEC)= 25
SWEEP SEGMENTS= 2
SMPL INT.(MV)= 1
R (OHM)= 2447
UC R (OHM)= 244

ANODIC:
PEAK POTENTIAL(MV)= +1170
PEAK CURRENT(A)= 2.7657E -6

CATHODIC:
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EXP. CONDITIONS:
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D SQUARE WAVE VOLTAMMETRY

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A.C. AMPLITUDE(MV)= 25
FREQUENCY(HZ)= 15
STEP E(MV)= 4
R (OHM)= 2302
UC R (OHM)= 230

EXP. RESULTS:
PEAK POTENTIAL(MV)= +1164
PEAK CURRENT(A)= 1.8696E -6
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Figure 1. Irreversible cyclic voltammogram (CV; top), reversible second harmonic ac voltammogram (SHACV; middle), and Osteryoung square wave voltammogram (OSWV; bottom) for the oxidation of 9-(methoxycarbonyl)fluorene in sulfolane/3-methylsulfolane (5%).

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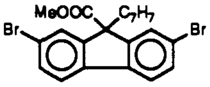
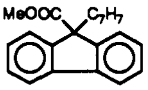
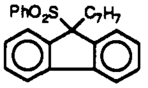
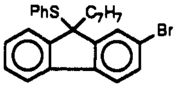
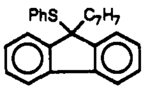
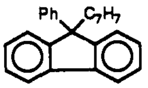
Table I. Thermodynamic Properties for Ions and Molecules Derived from Reaction, Oxidation, and Reduction of Tropylium and Fluorenide Ions

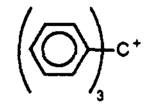

tropylium ion

$E_{1/2}(C^+) = -0.620 \pm 0.002$ V
$pK_{R^+} = 4.70$

compd	compd no.	$\Delta H_{het}[C-X]^a$ (kcal/mol)	$\Delta H_{homo}{}^a$ (kcal/mol)	$E_{ox}[C-X]^b$ (V)	$E_{red}[C-X]^b$ (V)	$\Delta H_{cleav}[C-X]^{\bullet+c}$ (kcal/mol)	$\Delta H_{cleav}[C-X]^{\bullet-c}$ (kcal/mol)
	1	19.45 ± 0.11	27.20	+1.519 ± 0.018	−1.000 ± 0.023	−22.17	10.69
	2	24.89 ± 0.53	26.44	+1.475 ± 0.020	−1.173 ± 0.015	−21.92	12.14
	3	27.17 ± 0.54	32.47	+1.632 ± 0.020	−1.540 ± 0.021	−19.50	5.95
	4	28.59 ± 0.12	26.05	+1.590 ± 0.023	−1.335 ± 0.020	−22.42	12.10
	5	30.52 ± 0.45	24.52	+1.439 ± 0.019	−1.370 ± 0.015	−23.00	13.23
	6	33.84 ± 0.32	22.79	+1.394 ± 0.025	−1.430 ± 0.020	−23.69	15.16

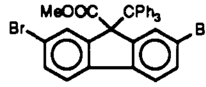
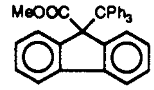
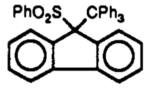
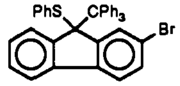
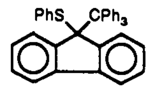
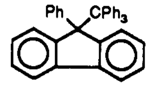
[a] Values from ref 2b. [b] Potentials referred to Ag/AgNO$_3$ electrode and measured in sulfolane/5% 3-methylsulfolane solvent system at 25 °C. [c] The error involved in these measurements is ca. 2 kcal/mol.

Table II. Thermodynamic Properties for Ions and Molecules Derived from Reaction, Oxidation, and Reduction of Triphenylmethylium and Fluorenide Ions



triphenylmethylium ion

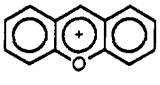
$E_{1/2}(C^+) = -0.133 \pm 0.007$ V
$pK_{R^+} = -6.63$

compd	compd no.	$\Delta H_{het}[C-X]^a$ (kcal/mol)	$\Delta G_{ET}{}^a$ (kcal/mol)	$\Delta H_{homo}{}^a$ (kcal/mol)	[AOP + CRP]	$E_{red}[C-X]^b$ (V)	$\Delta H_{cleav}[C-X]^{\bullet-c}$ (kcal/mol)
	7	19.76 ± 0.85	−3.53	16.23	14.54	−0.445 ± 0.010	12.57
	8	25.81 ± 0.42	−9.73	16.08	15.03	−0.727 ± 0.006	12.11
	9	28.35 ± 0.59	−5.97	22.38	18.98	−1.032 ± 0.013	7.62
	10	29.41 ± 0.52	−13.81	15.60	13.40	−0.850 ± 0.016	12.88
	11	33.61 ± 0.34	−17.27	16.34	12.96	−1.055 ± 0.015	12.35
	12	35.51 ± 0.56	−22.32	13.18	11.33	−1.059 ± 0.025	14.16

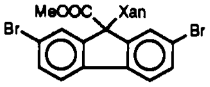
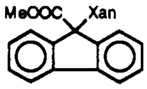
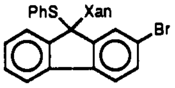
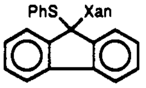
[a] Values from ref 2b. [b] Potentials referred to Ag/AgNO$_3$ electrode and measured in sulfolane/5% 3-methylsulfolane solvent system at 25 °C. [c] The maximum error involved in these measurements is ca. 2.0 kcal/mol.

chemical oxidation and reduction.[27-35] Important milestones were the recognition of radical anion chain processes in aromatic substitution,[36] a donor–acceptor approach to electrophilic aromatic substitution,[37] the use of amine radical cations in a variety of

Table III. Thermodynamic Properties for Ions and Molecules Derived from Reaction, Oxidation, and Reduction of Xanthylium and Fluorenide Ions

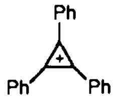

xanthylium ion

$E_{1/2}(C^+) = -0.347 \pm 0.010$ V
$pK_{R^+} = -0.84$

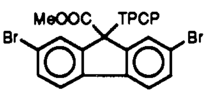
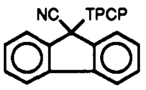
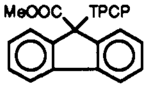
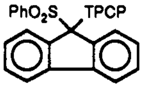
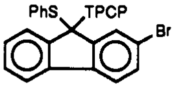
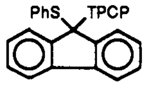
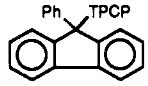
compd	compd no.	ΔH_{het}[C-X][a] (kcal/mol)	ΔG_{ET}[a] (kcal/mol)	ΔH_{homo}[a] (kcal/mol)	[AOP + CRP]	E_{ox}[C-X][b] (V)	E_{red}[C-X][b] (V)	ΔH_{cleav}-[C-X]$^{\bullet+}$ [c] (kcal/mol)	ΔH_{cleav}-[C-X]$^{\bullet-}$ [c] (kcal/mol)
	**13**	24.62 ± 1.02	1.41	26.03	10.4	+1.519 ± 0.018	-1.045 ± 0.010	-22.63	8.52
	**14**	27.33 ± 0.79	-4.80	22.53	9.91	+1.475 ± 0.020	-0.930 ± 0.015	-23.24	13.89
	**15**	30.13 ± 1.12	-8.88	21.25	12.0	+1.439 ± 0.019	-0.929 ± 0.018	-23.42	16.71
	**16**	33.03 ± 1.12	-12.34	20.69	11.5	+1.394 ± 0.025	-1.000 ± 0.010	-23.54	17.97

[a] Values from ref 2b. [b] Potentials referred to Ag/AgNO$_3$ electrode and measured in sulfolane/5% 3-methylsulfolane solvent system at 25 °C. [c] The error involved in these measurements is ca. 2 kcal/mol.

Table IV. Thermodynamic Properties for Ions and Molecules Derived from Reaction, Oxidation, and Reduction of Triphenylcyclopropenylium and Fluorenide Ions


triphenylcyclopropenylium ion

$E_{1/2}(C^+) = -1.304 \pm 0.003$ V
$pK_{R^+} = 3.10$

compd	compd no.	ΔH_{het}[C-X][a] (kcal/mol)	ΔG_{ET}[a] (kcal/mol)	ΔH_{homo}[a] (kcal/mol)	[AOP + CRP]	E_{ox}[C-X][b] (V)	E_{red}[C-X][b] (V)	ΔH_{cleav}-[C-X]$^{\bullet+}$ [c] (kcal/mol)	ΔH_{cleav}-[C-X]$^{\bullet-}$ [c] (kcal/mol)
	**17**	16.22 ± 0.10	23.48	39.70	28.1	+1.480 ± 0.011	-0.740 ± 0.010	-24.50	29.23
	**18**	19.56 ± 0.30	18.98	38.54	26.1	+1.469 ± 0.014	-0.827 ± 0.015	-25.41	30.56
	**19**	20.62 ± 0.12	17.27	37.89	28.6	+1.463 ± 0.013	-0.836 ± 0.010	-25.92	31.42
	**20**	22.23 ± 0.36	21.06	43.26	32.6	+1.517 ± 0.012	-1.128 ± 0.013	-21.79	26.29
	**21**	25.40 ± 0.50	13.19	38.59	27.0	+1.470 ± 0.010	-1.079 ± 0.012	-25.38	30.60
	**22**	27.49 ± 0.18	9.73	37.22	26.6	+1.461 ± 0.013	-1.117 ± 0.015	-26.54	31.80
	**23**	29.34 ± 0.28	4.68	34.02	24.9	-1.080 ± 0.012		34.51	

[a] Values from ref 2b. [b] Potentials referred to Ag/AgNO$_3$ electrode and measured in sulfolane/5% 3-methylsulfolane solvent system at 25 °C. [c] The error involved in these measurements is ca. 2 kcal/mol.

contexts,[33,38-40] and a recent proposal by Shaik and Pross[41] that a number of fundamental organic reaction mechanisms, e.g., S$_N$2 substitution, occur through single electron transfer followed by radical ion reactions.

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The chemistry of the radical anions is also fairly well understood and documented in literature.[36,42,43] Radical anions are intermediates in a variety of processes: dissolving metal reductions,[44] cathodic reduction,[45] excited-state quenching reactions,[35b] homogeneous redox reactions,[46] $S_{RN}2$ reactions,[36a,47] and nucleophilic substitutions.[48] Several techniques ranging from pulse radiolysis,[49] near-infrared spectroscopy,[50] derivative linear-sweep voltammetry,[51] and electron spin resonance spectroscopy[52] have been employed to study the characteristic properties of the radical anions. The theoretical[53] and experimental[3,50,54-56] aspects of the organic electron-transfer reactions of the radical anions have also been analyzed.

The unusually facile cleavage of radical ions, a commonplace observation in mass spectrometry,[16a] has stimulated a wide range of research on radical ion chemistry. In particular, studies of dibenzyl radical ions[57] and the related work by Maslak[3a,d,f] on a carefully developed series of dicumyls have demonstrated the facile cleavage on radical ions whose precursors are frequently employed as models for high-temperature thermolysis in the fossil fuel industries. In contrast to the dibenzyl and dicumyl series, the systems described here are unsymmetrically biased toward the formation of at least one resonance-stabilized ion.

Experimental Section

All the experimental techniques for purification and handling of materials as well as the calorimetric methods have been described elsewhere.[2b] The electrochemical measurements were carried out with a BAS 100A electrochemical analyzer in binary solvent mixtures of sulfolane and 5% 3-methylsulfolane. The preparation and purification of the solvent mixture have been described in our previous publications.[2b] The cyclic voltammetric (CV) and second harmonic alternating current voltammetric (SHACV) procedures and the experimental conditions have also been detailed.[2b] In those cases where consistent voltammetric responses could not be obtained by CV or SHACV, Osteryoung square wave voltammetry (OSWV) was used to determine the redox potentials.

The radical ions derived from the neutral molecules are much less stable than the cationic and the anionic species. In many cases, it was extremely difficult to obtain consistent voltammograms for them. However, with judicious application of the above voltammetric techniques, it was possible to obtain reproducible and symmetrical voltammetric responses for most of the neutral molecules and the radical ionic species studied. Furthermore, the results obtained by the three methods agreed to a remarkable degree even though cyclic voltammograms were very irreversible (Figure 1). In all cases, the ionic product of the radical ion cleavage was confirmed by oxidation or reduction of a bona fide sample.

Two methods were used to establish the electrochemistry of the neutral molecules. The redox potentials obtained by both the methods agreed very well (within ±15 mV).

(1) The compound was prepared in situ inside an ultrapure argon-filled drybox by reacting equimolar amounts of the carbenium ion and the anion in the binary solvent mixture.

(2) In a few cases, the neutral compound was prepared inside the drybox and isolated and electrochemical measurements were made on this isolated compound. In a typical experiment, 0.224 g (0.001 M) of 9-(methoxycarbonyl)fluorene in 5 mL of the solvent mixture was stirred with 0.12 g (0.003 M) of previously dried potassium hydride inside the drybox with slight warming for 30 min. The honey brown fluorescent salt was then filtered off. To this, 0.18 g (0.001 M) of tropylium tetrafluoroborate (Aldrich, twice recrystallized from acetonitrile) in 5 mL of the solvent mixture was added slowly till the solution became pale yellow or off white. The resulting solution was taken out of the drybox and poured into saturated aqueous NaCl solution and the resultant white emulsion was extracted into ether. The ether extracts were washed 4–5 times with water, dried over anhydrous $MgSO_4$, and left in the hood for 60 h. White crystals appeared on the solution and were filtered and dried; mp = 224–25 °C. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.08; H, 5.73; O, 10.19. Found: C, 84.07; H, 5.74; O, 10.18 (Galbraith).

For the electrochemical measurements involving the neutral fluorenes, an amount of the compound sufficient to make 10 mL of 3.0 mM solution was weighed into the electrochemical cell inside the drybox. Tetrabutylammonium tetrafluoroborate ($TBAF_4$; 99% pure, Aldrich, recrystallized four times from a 5:1 mixture of ether and ethanol and dried under vacuum at 64 °C for 24 h, 0.1 M) was placed in the cell and 10 mL of pure sulfolane/5% 3-methylsulfolane solvent mixture added to it. The solution was stirred for 30 min inside the drybox to ensure complete dissolution. It was then taken out of the drybox and flushed with ultrapure argon for 1 min, and electrochemical measurements were made by carrying out cyclic voltammetry (CV), second harmonic ac voltammetry (SHACV), or Osteryoung square wave voltammetry (OSWV). Routinely, a ferrocenium/ferrocene redox couple was used as the internal standard, and its redox potential was checked against the reference electrode before and after the experiments.

OSWV measurements were made at scan speeds of 60 mV/s (scan frequency 15 mV and step voltage 4 mV). The square wave voltammetric responses for most of the compounds are peak-shaped and highly symmetrical.

Results

Tables I–IV present all the data necessary to compare the energetics for bond rupture for twenty-three compounds prepared from the reaction of four resonance-stabilized carbenium ions with a series of substituted fluorenide ions at 25 °C in sulfolane containing 5% 3-methylsulfolane. In several cases, the extreme in-

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(44) (a) McOmie, J. F. W. *Protective Groups in Organic Chemistry*; Plenum Press: New York, 1973. (b) Muth, H.; Sauerbier, M. In *Houben-Weyl Methoden der Organische Chemie*; Georg Thieme: Stuttgart, 1980; Part 4/1c, Reduktion, Vol. 1. (c) Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981.

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(54) (a) Shultz, D. A.; Fox, M. A. *J. Org. Chem.* **1990**, *55*, 1047. (b) Andrieux, C. P.; Gélis, L.; Medebielle, M.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 3509.

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stability of the radical cation or radical anion produced by oxidation or reduction of the neutral molecule made it impossible to obtain a ΔH_{cleav} for the corresponding radical cation or radical anion. Accordingly, some tables are more extensive than others.

The data provided in each table, some of which were obtained from previous publications, are as follows: (1) ($E_{1/2}(C^+)$) is the half-wave reduction potential of the carbenium ions. (2) The pK_{R^+} values of the carbenium ions are derived from the equilibrium constants for ionization of the corresponding carbinol in aqueous sulfuric acid solutions.[58] (3) ΔH_{het}[C–X] is the heat of heterolysis of the neutral molecule derived from the heat of reaction of the carbenium ion with the fluorenide ion and with the sign changed.[2b] (4) ΔG_{ET} is the free energy of single electron transfer determined from the redox potentials of the carbenium ion and the fluorenide ion.[2b] This property when combined with ΔH_{het} provides the enthalpy of homolysis for the corresponding bond.[2b] (5) The sum [AOP + CRP] is a radical stabilization term derived from the acid oxidation potential of the substituted fluorene[2b,26] and the carbinol reduction potential of the carbinol precursor for the carbenium ion.[2b] (6) E_{ox}[C–X] is the oxidation potential of the neutral species C–X, leading to the corresponding radical cation. (7) E_{red}[C–X] is the corresponding reduction potential of the neutral species, leading to the formation of radical anions.

The redox potentials of the radical ions are measured by using the three voltammetric methods. There is a specific reason for using Osteryoung square wave voltammetry to supplement the results obtained by cyclic voltammetry and second harmonic ac voltammetry. Unlike CV, which is a dc technique involving a triangular wave form, and SHACV, which is a slow ac technique, Osteryoung square wave voltammetry (OSWV) involves the superimposition of a pulse train of opposing square wave impulses on a staircase wave form.[12] This technique has the following advantages over conventional CV.

(1) OSWV allows one to detect analytes even at concentrations lower than 10^{-8} M.

(2) It retains high discrimination against double-layer charging current. This is because the current samples are taken during the last portions of the forward and the reverse steps of the square wave where the interference due to double-layer charging current contributions is the least.

(3) Since the square wave voltammetric response is peak-shaped and in many cases symmetrical, it is useful for quick descriptions of electrochemical processes.

(4) Greater sampling of data points is possible by using this technique, and this enhances the efficiency and reliability of the potentials measured.

(5) Higher scan rates than CV permit voltammograms to be obtained over a wider potential range within 1 s.

(6) Recently, it has been shown that the reversible voltammetric response varies little with the shapes of electrodes used.[12c] This means that the square wave voltammograms have the same peak potential and shape, regardless of electrode geometry.

The agreement among the redox potentials obtained by the three totally different techniques is truly remarkable (Figure 1). This also gives added credibility to the electrochemical measurements done under irreversible conditions by us[2a,b,c] and other groups.[3,4,26] The oxidation potentials of the fluorenides are available from our previous studies[2a,b,c] and those of Bordwell's group.[26]

Finally, in the last two columns are the heats of cleavage for the radical cation and radical anion derived from C-X. The maximum error involved in the measurement of redox potentials of the radical ions and the ionic species is ±25 mV. As a consequence, the heats of cleavage of the radical ions can be estimated within ca. 1.5–2 kcal/mol, a reasonably good precision for our purposes.

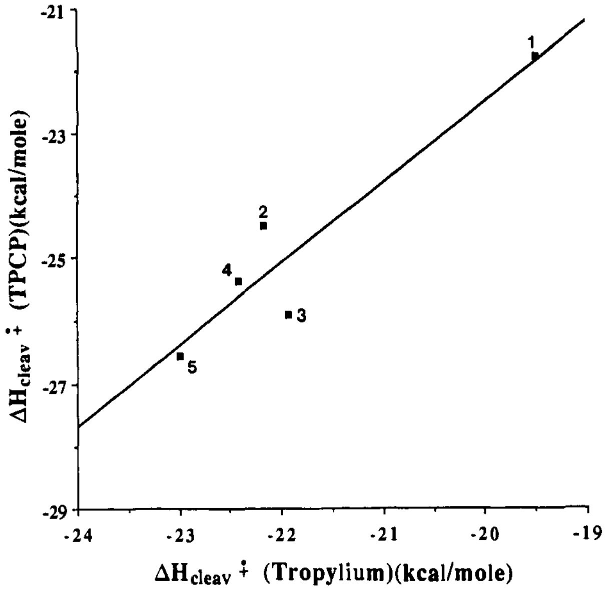

Figure 2. $\Delta H_{cleav}[C–X]^{\bullet+}$ for triphenylcyclopropenylium and tropylium fluorenide radical cations: (1) 9-(phenylsulfonyl)fluorenyl, (2) 2,7-dibromo-9-(methoxycarbonyl)fluorenyl, (3) 9-(methoxycarbonyl)fluorenyl, (4) 2-bromo-9-(thiophenyl)fluorenyl, (5) 9-(thiophenyl)fluorenyl. $\Delta H_{cleav^{\bullet+}}$ (TPCP) = 3.36 + 1.29$\Delta H_{cleav^{\bullet+}}$ (tropylium); R = 0.9393.

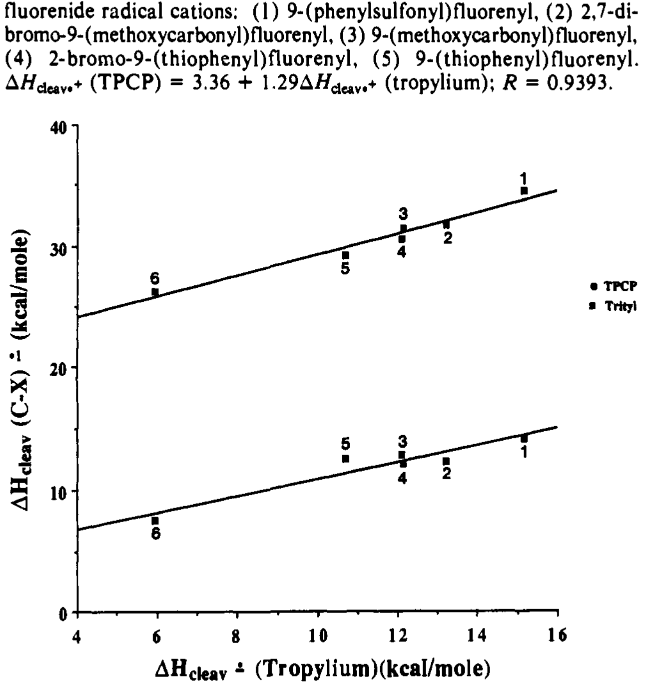

Figure 3. $\Delta H_{cleav}[C–X]^{\bullet-}$ for triphenylcyclopropenylium, trityl, and tropylium fluorenide radical anions: (1) 9-phenylfluorenyl, (2) 9-(thiophenyl)fluorenyl, (3) 2-bromo-9-(thiophenyl)fluorenyl, (4) 9-(methoxycarbonyl)fluorenyl, (5) 2,7-dibromo-9-(methoxycarbonyl)fluorenyl, (6) 9-(phenylsulfonyl)fluorenyl. $\Delta H_{cleav}{}^{\bullet-}$ (TPCP) = 20.7 + 0.86$\Delta H_{cleav}{}^{\bullet-}$ (tropylium); R = 0.9777. $\Delta H_{cleav}{}^{\bullet-}$ (trityl) = 4.12 + 0.68$\Delta H_{cleav}{}^{\bullet-}$ (tropylium); R = 0.9446.

Table V presents data used to derive the $pK_{HA^{\bullet+}}$s for the radical cations of the fluorenes. All of the pK_{HA}s of the parent fluorenes were determined by Bordwell's group in dimethyl sulfoxide using their indicator method.[59] The oxidation potentials of the substituted fluorenes and their derived anions were determined by us in sulfolane/3-methylsulfolane solvent system, which we assume, by virtue of dielectric constant and other properties,[60] should be virtually interchangeable with DMSO as a medium for determination of redox potentials. Support for this assumption is given by the agreement within experimental error between our $pK_{HA^{\bullet+}}$ values for fluorene and 9-phenylfluorene and those obtained by the Bordwell group.[26c] Bordwell has discussed the question of estimated errors for such data.[26c] It is interesting that although

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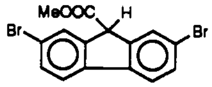
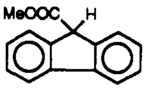
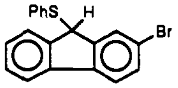
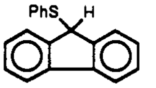
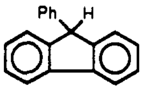
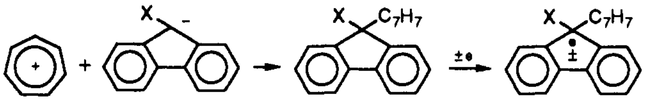
Table V. pK_{HA}s, $pK_{HA^{\bullet+}}$s, $E_{ox}(A^-)$, $E_{ox}(HA)$, and $\Delta G^{\bullet+}$ of Fluorenes

fluorene	compd no.	pK_a [a]	$E_{ox}(A^-)$ [b] (V)	$E_{ox}(HA)$ [b] (V)	$pK_{HA^{\bullet+}}$ [c]	$\Delta G^{\bullet+}$ [e] (kcal/mol)
	**24**	6.52	0.520 ± 0.003	2.262 ± 0.014	−22.8	−31.2
	**25**	10.4	0.251 ± 0.010	2.196 ± 0.015	−22.4	−30.7
	**26**	13.2	0.074 ± 0.002	2.181 ± 0.018	−22.3	−30.6
	**27**	15.4	−0.076 ± 0.004	2.159 ± 0.016	−22.2	−30.4
	**28**	17.9	−0.225 ± 0.010	2.156 ± 0.020	−22.2 [d]	−30.4

[a] Values from ref 59. [b] Potentials referred to SHE and measured in sulfolane/5% 3-methylsulfolane solvent system at 25 °C. [c] Radical cation acidities are calculated from Bordwell's equation, $pK_{HA^{\bullet+}} = pK_{HA} + 23.06/1.37\{E_{ox}(A^-) - E_{ox}(HA)\}$. All the values have an error of 0.1 $pK_{HA}{}^{\bullet+}$ units. [d] Bordwell obtained a value of −22 for this radical cation in DMSO (ref 4). [e] $\Delta G^{\bullet+} = 1.37pK_{HA^{\bullet+}}$.

Table VI. Correlation Coefficients for Plots of Various Properties of Tropylium and Fluorenide Ions, the Cleavage of the Molecules Formed from Them, and the Related Radical Ions



properties correlated	cc
ΔH_{het} vs pK_a	0.9942
ΔH_{het} vs $E_{1/2}$	0.9881
ΔH_{het} vs ΔG_{ET}	0.9941
$\Delta H_{cleav}{}^{\bullet+}$ vs ΔH_{homo}	0.9910
$\Delta H_{cleav}{}^{\bullet-}$ vs ΔH_{homo}	0.9963
$\Delta H_{cleav}{}^{\bullet+}$ vs [AOP + CRP]	0.9943
$\Delta H_{cleav}{}^{\bullet-}$ vs [AOP + CRP]	0.9725
$\Delta H_{cleav}{}^{\bullet+}$ vs $\Delta H_{cleav}{}^{\bullet-}$	0.9783
ΔH_{het} vs ΔH_{homo}	0.3855
$\Delta H_{cleav}{}^{\bullet+}$ vs ΔH_{het}	0.3895
$\Delta H_{cleav}{}^{\bullet-}$ vs ΔH_{het}	0.4612

the pK_{HA} and $E_{ox}(A^-)$ values cover wide ranges of 15.6 and 17.1 kcal/mol, respectively, there is relatively little variation in E_{ox}(HA). When all values are finally combined by using the thermodynamic cycle, there is a virtually complete compensation so that there is no recognizable structure–reactivity trend in the calculated values for $pK_{HA^{\bullet+}}$. This issue has been addressed carefully by Bordwell.[26c] In this respect, our results are in total agreement with his.

Discussion

Examination of ΔH_{cleav} values for the radical cations and radical anions in Tables I–IV shows a dramatic difference between the driving force for cleaving the radical cations as compared to the radical anions. For the 16 radical cations derived from tropylium, xanthylium and triphenylcyclopropenylium ions with the substituted fluorenes, $\Delta H_{cleav}[C\text{–}X]^{\bullet+}$ values are all exothermic and lie within the range of −26.54 to −19.50 kcal/mol. Unfortunately, the radical cations derived from the triphenylmethyl cation were

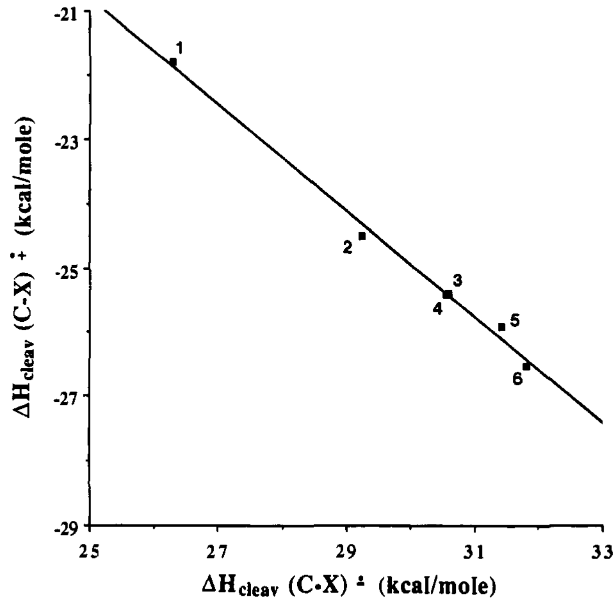


Figure 4. $\Delta H_{cleav}[C\text{–}X]^{\bullet+}$ vs $\Delta H_{cleav}[C\text{–}X]^{\bullet-}$ for triphenylcyclopropenylium fluorenides: (1) 9-(phenylsulfonyl)fluorenyl, (2) 2,7-dibromo-9-(methoxycarbonyl)fluorenyl, (3) 2-bromo-9-(thiophenyl)fluorenyl, (4) 9-cyanofluorenyl, (5) 9-(methoxycarbonyl)fluorenyl, (6) 9-(thiophenyl)fluorenyl. $\Delta H_{cleav}[C\text{–}X]^{\bullet+} = -0.06 - 0.83\Delta H_{cleav}[C\text{–}X]^{\bullet-}$; $R = 0.9978$.

Table VII. Slopes, Intercepts, and Correlation Coefficients for the Various Correlation Plots for the Radical Ionic Species Formed by the Cleavage of Neutral Compounds Formed between Fluorenides and Various Resonance-Stabilized Carbenium Ions[a]

	carbenium ion											
	$(C_7H_7)^+$			Ph_3C^+			(xanthylium)$^+$			(TPCP)$^+$		
correlation plot	*A*	*B*	cc	*A*	*B*	cc	*A*	*B*	cc	*A*	*B*	cc
$\Delta H_{cleav}{}^{\bullet+}$ vs ΔH_{homo}	+0.43	−33.6	0.9910				+0.17	−27.0	0.9993	+0.78	−55.4	0.9997
$\Delta H_{cleav}{}^{\bullet-}$ vs ΔH_{homo}	−0.95	+36.7	0.9963	−0.73	+24.1	0.9931	−1.74	+53.7	0.9958	−0.90	+65.4	0.9976
$\Delta H_{cleav}{}^{\bullet+}$ vs [AOP + CRP]	+0.55	−27.6	0.9943				−0.25	−20.5	0.5899	+0.63	−42.7	0.8835
$\Delta H_{cleav}{}^{\bullet-}$ vs [AOP + CRP]	−1.16	+23.2	0.9725	−0.82	+23.8	0.9584	+2.92	−17.8	0.6717	−0.89	+55.4	0.8844
$\Delta H_{cleav}{}^{\bullet+}$ vs $\Delta H_{cleav}{}^{\bullet-}$	−0.45	−16.9	0.9783				−0.10	−21.8	0.9935	−0.83	−0.06	0.9978

[a] $Y = AX + B$ where A = slope, B = Y intercept, and cc = correlation coefficient.

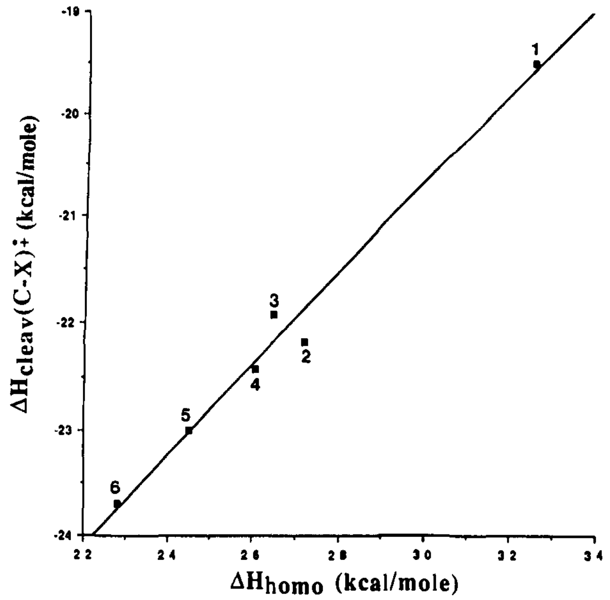


Figure 5. $\Delta H_{\rm cleav}[C-X]^{\bullet+}$ vs $\Delta H_{\rm homo}$ for the reaction products of fluorenides with tropylium ion: (1) 9-(phenylsulfonyl)fluorenyl, (2) 2,7-dibromo-9-(methoxycarbonyl)fluorenyl, (3) 9-(methoxycarbonyl)fluorenyl, (4) 2-bromo-9-(thiophenyl)fluorenyl, (5) 9-(thiophenyl)fluorenyl, (6) 9-phenylfluorenyl. $\Delta H_{\rm cleav}[C-X]^{\bullet+} = -33.6 + 0.43\Delta H_{\rm homo}$; $R = 0.9910$.

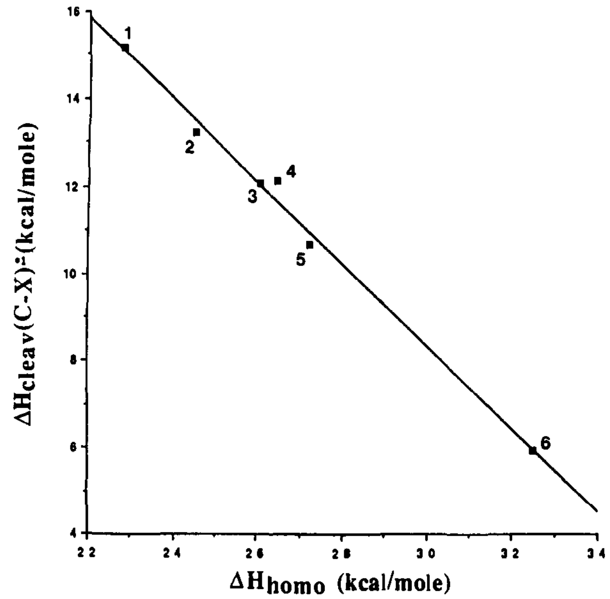


Figure 6. $\Delta H_{\rm cleav}[C-X]^{\bullet-}$ vs $\Delta H_{\rm homo}$ for the reaction products of fluorenides with tropylium ion: (1) 9-phenylfluorenyl, (2) 9-(thiophenyl)fluorenyl, (3) 2-bromo-9-(thiophenyl)fluorenyl, (4) 9-(methoxycarbonyl)fluorenyl, (5) 2,7-dibromo-9-(methoxycarbonyl)fluorenyl, (6) 9-(phenylsulfonyl)fluorenyl. $\Delta H_{\rm cleav}[C-X]^{\bullet-} = 36.7 - 0.95\Delta H_{\rm homo}$; $R = 0.9963$.

too unstable to permit measurement of their $E_{\rm ox}[C-X]$. There is a very strong exothermic driving force for rupture of the three sets of radical cations, but it is not directly related to the stabilities of the carbenium ions since the $\Delta H_{\rm cleav}[C-X]^{\bullet+}$ values for xanthylium and tropylium series are almost identical. They are less exothermic for the comparable compounds derived from triphenylcyclopropenylium ion, although its pK_{R^+} is closer to that of tropylium than it is to that for xanthylium. The three sets of $\Delta H_{\rm cleav}[C-X]^{\bullet+}$ correlate fairly well with each other with nearly unit slopes and $R \approx 0.94$ (see for example Figure 2).

$\Delta H_{\rm cleav}$ values for radical anions follow a totally different pattern. All 23 values are endothermic and within the series generated by each cation cover a much wider range than was found for the corresponding radical cations. There is a fairly good correlation among the $\Delta H_{\rm cleav}[C-X]^{\bullet-}$s of the four series of compounds (Figure 3).

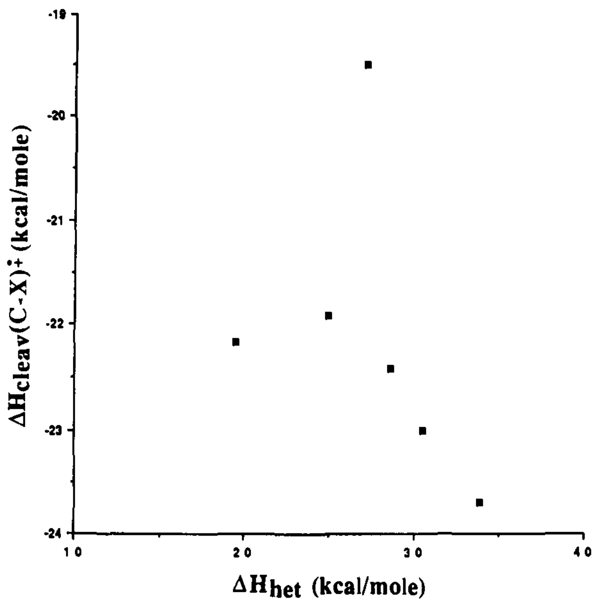


Figure 7. $\Delta H_{\rm cleav}[C-X]^{\bullet+}$ vs $\Delta H_{\rm het}$ for the reaction products of fluorenides with tropylium ion.

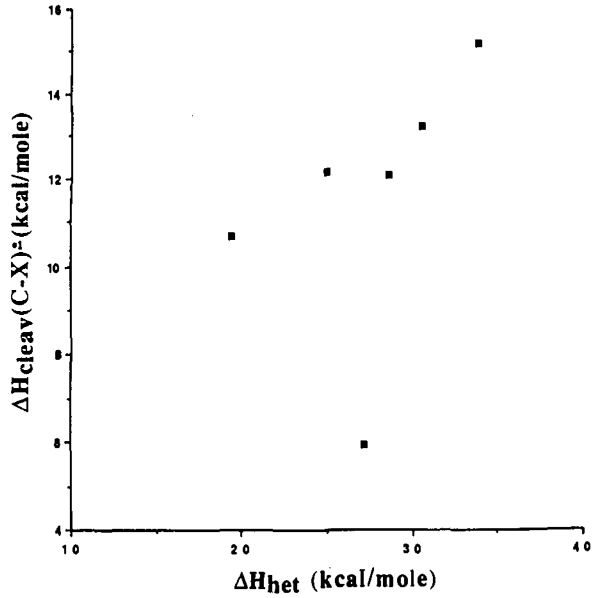


Figure 8. $\Delta H_{\rm cleav}[C-X]^{\bullet-}$ vs $\Delta H_{\rm het}$ for the reaction products of fluorenides with tropylium ion.

One may conclude from the overall comparison of these data that the driving force to cleave the radical cations is dominated by the relatively high stabilities of the tropylium, xanthylium, and triphenylcyclopropenylium ions, all of which are stable in dilute aqueous acid. In contrast, the driving force to cleave the radical anions to regenerate the substituted fluorenide ions and the radicals derived from the cations reflects the relative instability of these highly basic anions. This is understandable because they cannot be produced in any aqueous base system but require potassium dimsyl/DMSO solutions that are at least 28 pK_a units more basic than neutral water. Significantly, good (0.978) to excellent (0.997) correlations are produced from plots of $\Delta H_{\rm cleav}[C-X]^{\bullet+}$ vs $\Delta H_{\rm cleav}[C-X]^{\bullet-}$ for the three complete series of radical ions (Tables VI–VII) (Figure 4). Clearly, structural factors that influence the stabilities of the radical cations are proportional to those that affect the radical anions. Such good correlations would not be found if there were significant random errors in any of the various experimental values that are combined to produce the two sets of $\Delta H_{\rm cleav}$s.

$\Delta H_{\rm cleav}$s reflect the enthalpy differences between the radical cations or radical anions and their cleavage products so that no

Table VIII. Slopes, Intercepts, and Correlation Coefficients for the Various Correlation Plots for the Heats of Cleavage of Radical Ionic Species Formed between Fluorenides and Resonance-Stabilized Carbenium Ions[a]

correlation plots for	$\Delta H_{cleav}{}^{\bullet +}$ vs $\Delta H_{cleav}{}^{\bullet +}$			$\Delta H_{cleav}{}^{\bullet -}$ vs $\Delta H_{cleav}{}^{\bullet -}$		
	A	B	cc	A	B	cc
$(TPCP)^+$ vs $(C_7H_7)^+$	1.29	3.36	0.9393	0.86	20.7	0.9777
$(TPCP)^+$ vs $(Ph_3C)^+$				1.08	17.7	0.8788
$(TPCP)^+$ vs $(Xan)^+$	1.86	17.6	0.8691	0.23	27.5	0.8379
$(Ph_3C)^+$ vs $(C_7H_7)^+$				0.68	4.12	0.9446
$(C_7H_7)^+$ vs $(Xan)^+$	0.65	−7.18	0.5723	0.23	8.73	0.9362
$(Ph_3C)^+$ vs $(Xan)^+$				0.37	9.69	0.0286

[a] $Y = AX + B$ where A = slope, B = Y intercept, and cc = correlation coefficient.

definitive analysis in simple terms of the product cations, anions, or radicals is possible without considering the effect of structure on the stability of each initial radical cation or radical anion. The best source of such data is the oxidation and reduction potentials E_{ox}[C–X] and E_{red}[C–X], which represent the energies required to convert the neutral molecules to their radical ions. E_{ox}[C–X]s are remarkably similar for the compounds derived from the three cations, indicating that the variation in stability within each series of E_{ox}[C–X] is determined almost entirely by the fluorenyl portions of the radical cations. In contrast, E_{red}[C–X] values vary considerably from one series to another, indicating the important influence of the cationic portion of the molecule on the stability of the radical anion.

An interesting comparison can be made between the ΔH_{cleav}[C–X]$^{\bullet +}$ values and the acidities of the radical cations of the corresponding fluorenes as shown in Table V. Here the leaving group is a proton rather than a resonance-stabilized carbenium ion. Yet the highly exergonic energies of cleavages of these radical cations, of the order of −30 kcal/mol, are comparable to the calculated enthalpies of cleavage for the more complex radical cations derived from the carbenium ion systems.

Relation of ΔH_{cleav}s of Radical Ions to ΔH_{het} and ΔH_{homo} of Neutral Molecules. A radical ion is a charged radical and cleaves to form an ion and a radical. A natural question is whether the ΔH_{cleav}s of a series of radical ions are modeled better by the ΔH_{het}s or ΔH_{homo}s of their parent neutrals.

Figures 5–8 show clearly that ΔH_{cleav}s of the radical ions correlate much better with ΔH_{homo} than ΔH_{het} for the tropylium fluorenides and their radical ions. Equivalent correlations were obtained for the three other sets of compounds in Tables II–IV (Table VII). ΔH_{cleav}s for the radical ionic species for all the compounds except those derived from xanthylium ion correlate fairly well when plotted against [AOP + CRP] (Table VII). These anion oxidation potentials and cation reduction potentials are the homolytic bond dissociation energies of the acidic carbon–hydrogen bonds of the substituted fluorenes and the carbon–oxygen bonds of parent carbinols of the carbenium ions. We have referred to the limitations of using the CRP as a model for cleavage of carbon–carbon bonds elsewhere.[2b,c]

Previous reports in this series have articulated a simple rule: *Properties which involve the gain or loss of charge correlate with each other, and those that involve no change of charge correlate with each other but no correlation is found between the two sets of properties.* Tables VI–VIII depict a wide variety of correlations that validate this rule for this series of compounds. It remains to be seen how general it is for other types of systems. In the present case, ΔH_{cleav} values for both types of radical ions involve the conversion of a charged species into a charged species plus a neutral radical. This is similar to homolysis where there is neither gain nor loss of charge. Hence, correlation of ΔH_{cleav} with ΔH_{homo} is to be expected and is found.

Assuming the difference in the redox potentials between the neutral molecule C–X and the corresponding radicals derived from it to be a constant within a series of closely related compounds, Maslak[3] has shown a linear relationship between the free energies of bond activation for homolysis and mesolysis. This is quite similar to what we observe in the present study.

The fact that the slopes of plots of ΔH_{cleav} for the radical cations vs ΔH_{homo} of the neutral molecules are all positive merely shows that the effect of substitution on the fluorenyl radical is the same whether it is derived from the molecule or its radical cation. Likewise the negative slopes for plots of ΔH_{cleav} of the radical anions versus ΔH_{homo} for the corresponding neutral molecules means that the general effect of substitution in the fluorenide ions is in the opposite direction from the one on the respective radicals. However, if the only effect of fluorenyl substitution were on the product anions and radicals, all of the plots for ΔH_{cleav} for the various sets of radical anions vs ΔH_{homo} of their neutral molecules would have the same slope. The fact that they do not implies an important contribution of the fluorenyl substituents to the stabilities of the series of radical anions that are the initial states for the cleavage processes. The same may be true for the corresponding plots involving the radical cations.

The extreme instability of radical cations and radical anions has been noted by others.[3,15,16,26–30,51,54,56,61] The *exothermic heats of cleavage* for the radical cations in Tables I–IV demonstrate that these species are thermodynamically unstable as bonded compounds under these conditions and must cleave almost as soon as the electron is removed at the electrode. Maslak[3] and Camaioni[57] have noted the very low kinetic barriers associated with exothermic heats of cleavage for radical ions. In the present case, it is only reasonable that the product will be a very stable carbenium ion and a substituted fluorenyl radical rather than the alternative tropylium radical and the substituted fluorenyl cation. Correspondingly, fluorenide ions and relatively unstable radicals are formed by cleavage of the radical anions as shown by electrochemical analysis of the products.

The radical anions are much more stable than the corresponding radical cations, and the neutral molecules are mostly more stable thermodynamically than the radical anions. However, the latter are kinetically highly unstable as shown by irreversible cyclic voltammograms. It is interesting that, in several cases, ΔH_{cleav}[C–X]$^{\bullet -}$ is actually considerably more endothermic than either ΔH_{homo} or ΔH_{het} for C–X, the neutral molecule. Obviously for these systems, there are some enormous discrepancies between thermodynamics and kinetics of bond cleavage.

Electrochemical methods have been used to degrade a wide variety of coals and other polymers.[62–70] The strategy described here provides an entree to a complete thermochemical development of the relation between the various modes of cleavage for the molecules which can be made through coordination of cations and anions and for the related radical ions.

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