(dd, J = 5.2 and 11.8 Hz, 1 H), 2.16-2.35 (m, 1 H), 4.932 (d, J = 5.1 Hz, 1 H), 6.98-8.05 (m, 15 H). Anal. Calcd for $C_{29}H_{39}NSi_2$: C, 76.08; H, 8.59; N, 3.06. Found: C, 75.90; H, 8.85; N, 3.03.

X-ray Crystal Structure Analysis of 1. Crystal data: $C_{29}H_{39}NSi_2$, MW = 457.8, monoclinic, space group *Pn*, a = 13.407 (4) Å, b = 8.961 (5) Å, c = 11.637 (4) Å, α = 90.06 (3)°, β = 97.93 (3)°, γ = 89.96 (3)°, U = 1384.7 (4) Å^3, Z = 2, D_c = 1.10 g/cm^3, Mo Kα radiation (λ = 0.71069 Å), μ = 1.09 cm^{-1}. Intensity data were measured on a Mac Science MXC[3] diffractometer using an ω-2θ scan technique, and 3202 unique reflections within $3 \leq 2\theta \leq 55°$ were collected. The structure was solved by the direct method[10] and refined anisotropically by the full-matrix least-squares to R = 0.054, R_w = 0.042, and S = 1.31 for 3049 reflections. The thermal parameter of each hydrogen atom was assumed to be isotropic and equal to that of the bonded atom.

Thermal Decomposition of 2. A mixture of **2** (37.6 mg, 0.113 mmol) and toluene-d_8 (0.8 mL) was placed in an NMR tube, degassed at -78 °C, sealed, and heated at 204 °C. The progress of the decomposition was monitored occasionally by ^{1}H NMR spectroscopy. After 92 h, NMR showed the complete disappearance of **2** and formation of (*E*)-1-phenyl-3-methyl-1-butene (**4**) and 1,3-bis(*tert*-butyldimethylsilyl)-2,2,4,4-tetramethyl-1,3-diaza-2,4-disilacyclobutane (**5**) in 99% and 90% yields, respectively. The two products were isolated by preparative GLC (column temperature 150-200 °C). **4**: Retention time on GLC at 150 °C, 7.0 min; ^{1}H NMR (C_6D_6) δ 1.029 (d, J = 6.8 Hz, 6 H), 2.22-2.39 (m, 1 H), 6.100 (dd, J = 6.8 and 16.0 Hz, 1 H), 6.336 (d, J = 15.6 Hz, 1 H), 6.92-7.44 (m, 5 H). **5**: Retention time on GLC at 200 °C, 11.5 min; mp 43-44 °C;[11] ^{1}H NMR (standard TMS) δ 0.056 (s, 12 H), 0.372 (s, 12 H), 0.955 (s, 18 H);[9] mass spectrum (m/e) 374 (M$^+$, very weak).

Thermal Decomposition of 2 in the Presence of Ethoxytrimethylsilane. A degassed mixture of **2** (72.2 mg, 0.216 mmol), ethoxytrimethylsilane (170 μL, 1.080 mmol), and toluene-d_8 (0.9 mL) was heated in an NMR tube at 204 °C for 149 h. Two products, **4** and (*tert*-butyldimethylsilyl)(ethoxydimethylsilyl)(trimethylsilyl)amine (**6**), were formed in >99% and 94% yields, respectively, by NMR and were isolated by GLC at 180 °C. **6**: Retention time on GLC, 9 min; ^{1}H NMR ($C_6D_5CD_3$) δ 0.438 (s, 6 H), 0.484 (s, 6 H), 0.508 (s, 9 H), 1.233 (s, 9 H), 1.310 (t, J = 6.8 Hz, 3 H), 3.673 (q, J = 6.8 Hz, 2 H); exact mass calcd for $C_{13}H_{35}NOSi_3$ 305.2025, found 305.1997.

Kinetics Studies. A weighed sample of a 1-aza-2-silacyclobutane derivative (0.1-0.2 mmol) was dissolved in toluene-d_8 (0.8 mL) in an NMR tube. The mixture was degassed, sealed, and heated at 204 °C (four different temperatures for **2** as listed in Table **II**). The extent of the decomposition was followed by ^{1}H NMR by measuring relative intensities of signal due to one proton on the 4-position in the ring to the aromatic proton signals, except **11** where 1 molar equiv of benzene was added as the internal standard. ^{1}H NMR spectra were recorded on a Varian VXR200 spectrometer. The data were analyzed by the first-order rate law.

Acknowledgment. We thank the Ministry of Education, Science, and Culture, Japan, for a Grant-in-Aid for Special Project Research (No. 01649005).

Registry No. 1, 137363-31-6; **2**, 137363-32-7; **4**, 15325-61-8; **5**, 108148-64-7; **6**, 137363-34-9; **7**, 127209-39-6; **8**, 127209-38-5; **9**, 127209-44-3; **10**, 127209-40-9; **11**, 127209-41-0; **16**, 127209-35-2; **17**, 137393-30-7; **18**, 137363-33-8; Pt[{(CH$_2$=CH)Me$_2$Si}$_2$O]$_2$, 81032-58-8; HMe$_2$SiCl, 1066-35-9; *t*-BuMe$_2$SiCl, 18162-48-6; HPh$_2$SiCl, 1631-83-0; Me$_3$SiOEt, 1825-62-3; (*E*)-PhCH=CHMe, 873-66-5; (*Z*)-PhCH=CHMe, 766-90-5; PhCH=CMe$_2$, 768-49-0; cyclohexene, 110-83-8.

Supplementary Material Available: Tables S-I to S-III giving atomic coordinates, thermal parameters, full data of bond distances and angles for **1** (3 pages). Ordering information is given on any current masthead page.

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Heterolysis, Homolysis, and Cleavage Energies for the Cation Radicals of Some Carbon-Sulfur Bonds

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Abstract: Methods described previously for obtaining enthalpies of heterolysis (ΔH_{het}) and homolysis (ΔH_{homo}) for the cleavage of carbon-carbon and carbon-oxygen bonds to produce resonance-stabilized carbenium ions, anions, and radicals are extended to the study of some carbon-sulfur bonds. Titration calorimetry was used to obtain the heats of heterolysis. Cyclic voltammetry (CV), second harmonic ac voltammetry (SHACV), and Osteryoung square wave voltammetry (OSWV) were used to determine the redox potentials of the ions. Reversible potentials were obtained with considerable difficulty. The entropies of single-electron transfer were found to be negligible. A wide variety of correlations were tested between ΔH_{het} and ΔH_{homo}. These two properties showed no correlation with each other, but ΔH_{het} correlated well with properties for which neutral species are converted into ions or vice versa, such as the redox potentials of both types of ions, the pK_{HA}s of the anions, or the free energies of electron transfer (ΔG_{ET}). The enthalpies of cleavage (ΔH_{cleav}) of the radical cations derived from the neutral compounds prepared by the reactions of these thiophenoxides with five resonance-stabilized carbenium ions were determined by electrochemical oxidations. Radical anions derived from these compounds are too reactive and unstable to be studied. Excellent correlations were obtained between the ΔH_{cleav}s of the radical cations 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 of the same neutral compounds. The rule that all properties associated with processes which involve loss or gain of charge (e.g., heterolysis, pK_a, $E_{ox}(X^-)$) correlate with each other but not with properties associated with processes in which there is no change of charge (e.g., homolysis, cleavage) was confirmed, but a few exceptions were noted.

Introduction

The various problems associated with sulfur as a component element in coal have made its removal an important objective for coal chemists.[1-4] Basic information concerning the chemistry of organosulfur compounds is vital for the design of new coal desulfurization reactions and also for the environmentally effective

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Table I. Redox Potentials (V) of Thiophenoxides in Sulfolane/3-Methylsulfolane (5%)

parent thiophenol	E_{ox}[a]	$E_{1/2}$[a]	technique and conditions[c]
4-nitrothiophenol	+0.083 ± 0.003	−0.015 ± 0.005	SHACV, Pt electrode, 88 °C/178 °C, ac amplitude 100 mV, frequency 25 Hz
4-bromothiophenol	−0.264 ± 0.005	−0.280 ± 0.004	SHACV, Pt electrode, 2 °C/92 °C, ac amplitude 60 mV, frequency 25 Hz
4-chlorothiophenol	−0.326 ± 0.004	−0.380 ± 0.009	SHACV, Pt electrode, 2 °C/92 °C, ac amplitude 80 mV, frequency 25 Hz
thiophenol	−0.370 ± 0.004	−0.431 ± 0.005	SHACV, Pt electrode, 8 °C/98 °C, ac amplitude 100 mV, frequency 25 Hz
4-methylthiophenol	−0.465 ± 0.004	−0.495 ± 0.005	SHACV, Pt electrode, 6 °C/96 °C, ac amplitude 60 mV, frequency 25 Hz
4-methoxythiophenol	−0.530 ± 0.003	−0.540 ± 0.004	SHACV, Pt electrode, 6 °C/96 °C, ac amplitude 50 mV, frequency 25 Hz

[a] All E_{ox} values obtained by CV at a scan rate of 25 mV/s under an Argon blanket. [b] SHACV scan rate is 5 mV/s. All values reported vs ferrocenium/ferrocene $E_{1/2}$ values as obtained under identical conditions. All solutions are 1.5–6.0 mM in anion concentration. [c] All values obtained at 25 °C using a $Ag/AgNO_3$ reference electrode and Pt auxiliary electrode. Counterion is K^+.

Scheme I

$$C\text{–}X \rightleftharpoons C^+ + X^- \quad \Delta H_{hel} \qquad (1)$$

X = S

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

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

$$C\text{–}X \rightleftharpoons C^\bullet + X^\bullet \quad \Delta H_{homo} \qquad (4)$$

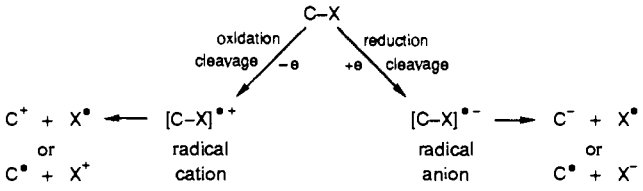
$$\Delta H_{homo} = \Delta H_{hel} + 23.06[E_{ox}X^- - E_{red}C^+] \qquad (5)$$

utilization of coal.[5] Several models have been proposed for the macrostructure of coal.[6] In the most widely accepted aromatic/hydroaromatic model for coal, the basic structure consists of aromatic and hydroaromatic building blocks, with heteroatoms like oxygen, sulfur, and nitrogen in various functional groups at their edges.[6,7] The detailed characterization of coal degradation products is a prime requirement for the development of an efficient coal liquefaction technology.[8] The precursor materials from which coals are formed contain various types of carbon–sulfur linkages.[9] Thiophenols and thiophenes form an integral part of the infrastructure of xylem tissue from degraded wood and coalified logs,[10,11] and the majority of the organic sulfur in high-ranked coals has been shown to be thiophenolic.[7,11,12,13]

Since all chemical reactions of covalently bonded molecules take place through the redistribution of bonding electron pairs, it is required that the cleavage of single bonds in neutral molecules must occur either heterolytically to produce ions or homolytically to produce radicals[14] and that these two processes be related through electron transfer (Scheme I).

Reliable heats of heterolysis (ΔH_{hel}) and homolysis (ΔH_{homo}) should be primary data for predicting chemical reactivity. Yet, there is a relative paucity of reliable quantitative data in the literature.[15-27] This is mainly due to the fact that the ions and

Scheme II



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

$$[C\text{–}X]^{\bullet+} + e^- \longrightarrow C\text{–}X \quad -E_{ox}(CX)$$

$$C\text{–}X \longrightarrow C^+ + X^- \quad \Delta H_{hel}(CX)$$

$$X^- - e^- \longrightarrow X^\bullet \quad E_{oxo}(X^-)$$

$$[C\text{–}X]^{\bullet+} \longrightarrow C^+ + X^\bullet \quad \Delta H_{cleav}(CX^{\bullet+})$$

$$\text{Thus: } \Delta H_{cleav}(CX^{\bullet+}) = \Delta H_{hel}(CX) + 23.06[E_{ox}X^- - E_{ox}(CX)] \qquad (6)$$

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

$$[C\text{–}X]^{\bullet-} - e^- \longrightarrow C\text{–}X \quad E_{red}(CX)$$

$$C\text{–}X \longrightarrow C^+ + X^- \quad \Delta H_{hel}(CX)$$

$$C^+ + e^- \longrightarrow C^\bullet \quad E_{red}C^\bullet$$

$$[C\text{–}X]^{\bullet-} \longrightarrow C^\bullet + X^- \quad \Delta H_{cleav}(CX^{\bullet-})$$

$$\text{Thus: } \Delta H_{cleav}(CX^{\bullet-}) = \Delta H_{hel}(CX) + 23.06\{E_{red}(CX) - E_{red}C^+\} \qquad (7)$$

radicals produced by bond cleavage undergo rapid and highly exothermic secondary reactions whose heat components cannot be separated easily from the initial bond-cleavage energies. Recently we have determined ΔH_{hel}s for C–C, C–O, C–N, and C–S bonds by titration calorimetry using resonance-stabilized ions.[28] The experiments have been carried out in an appropriate

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solvent mixture, such as sulfolane/5% 3-methylsulfolane in which all of the species are stable enough to be handled at high dilution at ambient temperature.[29,30] ΔH_{hetS} were converted to the corresponding ΔH_{homoS} by combination with the free energies of single-electron transfer (ΔG_{ET}) obtained from the redox potentials of the carbenium ions and the anions (Scheme I).[31,32] Analogous thermodynamic cycles have been proposed by Brauman,[33] Arnold,[34] Friedrich,[35] and Bordwell[36] for the determination of bond dissociation energies (BDEs) of bonds between various atoms and hydrogen by combination of their pK_as and anion oxidation potentials.

We have applied this thermodynamic cycle to 70 carbon–carbon bonds[31] and 60 carbon–oxygen bonds.[32] Although the derived ΔH_{hetS} and ΔH_{homoS} did not correlate with each other, each of them correlated with several other properties, depending only on whether or not a change of charge occurred in the process.[31,32] For example, ΔH_{hetS} correlated with redox potentials, single-electron-transfer energies, and the pK_as of the acids from which the anions were generated.

On the other hand, a dichotomy was observed in the behavior of the carbanions and the phenoxides with respect to the correlations involving pK_{R^+} values of the carbenium ions. While poor correlations were obtained when pK_{R^+} was used to represent the stabilization energies for the carbenium ions in the case of carbanions,[31] the heats of heterolysis of the carbenium ions with phenoxides were predicted well by a general equation that employed the pK_{R^+} of the carbenium ion without any modification and the pK_a of the phenol.[32] It is argued that the improvement is consistent with the fact that the cleavage of carbon–oxygen bonds of the triaryl carbinols in aqueous H_2SO_4 used to establish the pK_{R^+} stability scale[37] is a much more appropriate model for the heterolysis of carbon–oxygen bonds in sulfolane at 25 °C than it is for the cleavage of carbon–carbon bonds under the same conditions.[32]

In order to extend our methodology to the determination of heterolytic and homolytic energies of cleavage of some representative carbon–sulfur bonds, reactions of the previously studied carbenium ions with a series of substituted thiophenoxides[28] were examined with the same techniques and conditions as those used in our previous studies. Using a modified thermodynamic cycle (Scheme II), we have determined the enthalpies of cleavage of the radical cations and radical anions derived from the same series of neutral compounds[38] whose heats of heterolysis and homolysis are available from our previous studies.[31,32] We have extended this methodology to the reactions of six thiophenoxides with five resonance-stabilized carbenium ions.

Experimental Methods

The calorimetric and electrochemical techniques were the same as those described earlier.[31,32] The reduction potentials of the carbenium ions have also been reported.[31] Figure 1 compares an ordinary cyclic voltammogram (CV) to a second harmonic ac voltammogram (SHACV) for a typical thiophenoxide ion. Derived values of E_{ox} and $E_{1/2}$ are listed in Table I for the thiophenoxides studied along with the experimental conditions for obtaining them. The preparations of the various compounds have been detailed elsewhere.[28] The oxidation potentials of the radical cations derived from the neutral compounds formed between the thiophenoxides and the carbenium ions could not be studied by either CV or SHACV. Hence, a faster and much more efficient technique such as Osteryoung square wave voltammetry (OSWV) had to be employed in most of the cases. Unlike CV, which is a dc technique involving a triangular wave form, and SHACV, which is a slow ac technique, OSWV involves the superimposition of a pulse train of opposing square wave impulses on a staircase wave form. The advantages of this method over the conventional CV and SHACV are well-documented.[38,39] The radical anions derived from these neutral compounds are so unstable that they cannot be studied by any of these voltammetric techniques. The experimental methods used for the determination of the oxidation potentials of the radical cations are discussed elsewhere.[38] CV and SHACV gave meaningful voltammetric responses only in the case of thiophenoxides and some of the neutral compounds. However, consistently symmetric voltammetric responses were obtained for all of the species using OSWV. Figure 2 demonstrates the reasonably good agreement among the oxidation potentials obtained by the three totally different voltammetric methods.

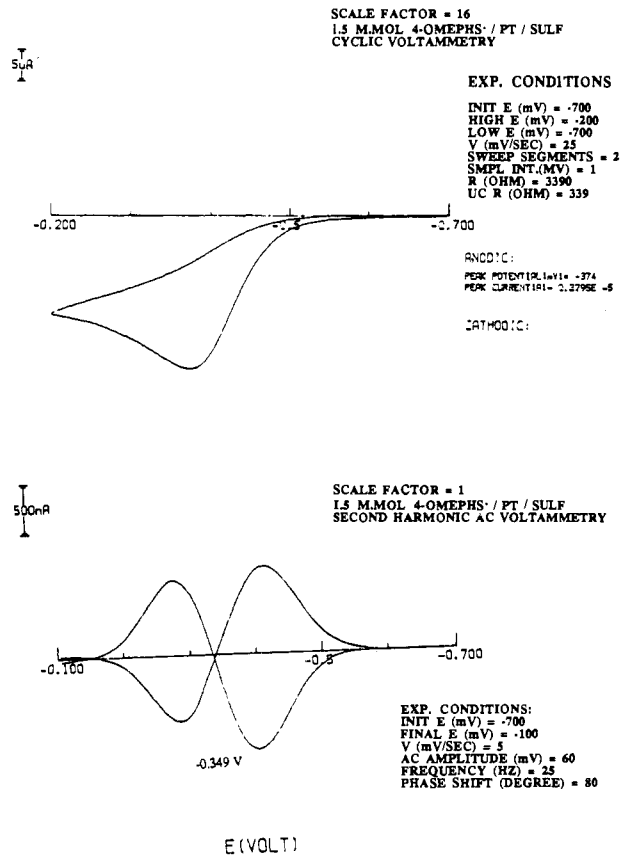

Figure 1. Irreversible cyclic voltammogram (CV, top) and reversible second harmonic ac voltammogram (SHACV, bottom) for the oxidation of 4-methoxythiophenoxide in sulfolane/3-methylsulfolane (5%) at 25 °C.

Results

Figure 3 demonstrates that the $E_{1/2}$ values of thiophenoxides vary linearly with E_{ox} values, with a slope of 0.997. Figure 4 shows a fair correlation between the $E_{1/2}$ values and the pK_{HA}s of the thiophenoxides in DMSO.[40] This apparent "linear" correlation for the 4-substituted thiophenoxides is probably a consequence

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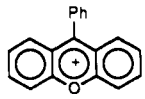
Table II. Heats of Heterolysis and Homolysis, Free Energies of Electron Transfer, Bond Dissociation Energies, (kcal/mol), AOPs, and CRP for Reactions of Trityl Cation[a] with Thiophenoxides in Sulfolane/3-Methylsulfolane (5%) at 25 °C

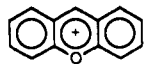
thiophenol	pK_a[b]	$E_{1/2}$, V[c]	AOP[d]	ΔH_{het}[e]	ΔG_{et}	ΔH_{homo}[f]	BDE[g]
4-nitrothiophenol	5.48	−0.015 ± 0.005	7.16	23.34 ± 0.37	2.72 ± 0.20	26.06 ± 0.42	81.6
4-bromothiophenol	8.98	−0.280 ± 0.004	5.85	26.87 ± 0.26	−3.39 ± 0.19	23.48 ± 0.32	80.2
4-chlorothiophenol	9.30	−0.380 ± 0.009	3.98	27.53 ± 0.41	−5.70 ± 0.26	21.83 ± 0.49	78.4
thiophenol	10.24	−0.431 ± 0.005	4.09	29.25 ± 0.63	−6.87 ± 0.20	22.38 ± 0.66	78.5
4-methylthiophenol	10.82	−0.495 ± 0.005	3.41	29.90 ± 0.35	−8.35 ± 0.20	21.55 ± 0.40	77.8
4-methoxythiophenol	11.19	−0.540 ± 0.004	2.88	31.92 ± 0.47	−11.14 ± 0.19	20.78 ± 0.51	77.3

[a] pK_{R^+} = −6.63, CRP = 12.2, $E_{1/2}(C^+)$ = −0.133 ± 0.007 V. [b] Values from ref 40. [c] Measured in a BAS-100A electrochemical analyzer in sulfolane/3-methylsulfolane at 25 °C by cyclic voltammetry or second harmonic ac voltammetry. [d] AOP = $1.37pK_a + 23.06E_{1/2}$. [e] ΔH_{het} measured in a calorimeter at 25 °C using $\Delta H_{het} = \Delta H_{rxn}$ (kcal/mol). [f] Calculated using the equation, $\Delta H_{homo} = \Delta H_{het} + \Delta G_{ET}$ where $\Delta G_{ET} = 23.06\,[E_{1/2}(S^-) - E_{1/2}(C^+)]$. [g] BDE = $1.37pK_a + 23.06E_{ox}(S^-) + 55.86$.

Table III. Heats of Heterolysis and Homolysis, Free Energies of Electron Transfer (kcal/mol), and CRPs for Reactions of 9-Phenylxanthylium and Xanthylium Ions with Thiophenoxides in Sulfolane/3-Methylsulfolane (5%) at 25 °C



9-phenylxanthylium[a]



xanthylium[b]

parent thiophenol	ΔH_{het}	ΔG_{het}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
4-nitrothiophenol	18.33 ± 0.20	7.77 ± 0.20	26.10 ± 0.28	21.66 ± 0.33	7.66 ± 0.26	29.32 ± 0.42
4-bromothiophenol	23.05 ± 0.32	1.66 ± 0.19	24.71 ± 0.37	24.70 ± 0.24	1.55 ± 0.25	26.25 ± 0.35
4-chlorothiophenol	24.36 ± 0.42	−0.65 ± 0.26	23.71 ± 0.49	25.87 ± 0.16	−0.76 ± 0.31	25.11 ± 0.35
thiophenol	26.11 ± 0.35	−1.82 ± 0.20	24.29 ± 0.40	26.43 ± 0.38	−1.94 ± 0.26	24.49 ± 0.46
4-methylthiophenyl	26.94 ± 0.19	−3.30 ± 0.20	23.64 ± 0.28	27.16 ± 0.34	−3.41 ± 0.26	23.75 ± 0.43
4-methoxythiophenol	27.85 ± 0.18	−4.34 ± 0.19	23.51 ± 0.26	27.67 ± 0.75	−4.45 ± 0.25	23.22 ± 0.79

[a] pK_{R^+} = 1.1, CRP = 6.84, $E_{1/2}(C^+)$ = −0.352 ± 0.007 V. [b] pK_{R^+} = −0.85, CRP = 9.15, $E_{1/2}(C^+)$ = −0.347 ± 0.010 V.

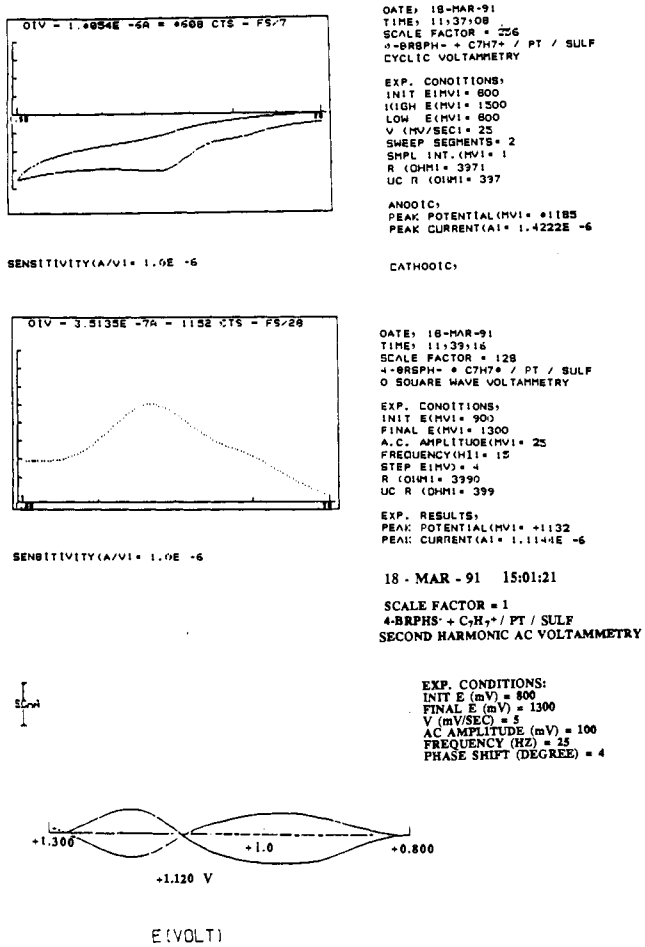


Figure 2. Irreversible cyclic voltammogram (CV, top), symmetrical Osteryoung square wave voltammogram (OSWV, middle), and reversible second harmonic ac voltammogram (SHACV, bottom) for the radical cations derived from the neutral compound formed between 4-bromothiophenoxide and tropylium ion in sulfolane/3-methylsulfolane (5%) at 25 °C.

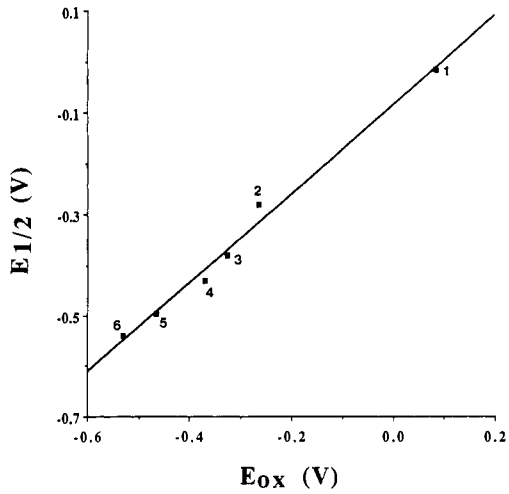
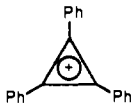


Figure 3. Plot of reversible oxidation potential ($E_{1/2}$) obtained by SHACV vs the irreversible oxidation potential (E_{ox}) obtained by CV for the thiophenoxides in sulfolane/3-methylsulfolane (5%) at 25 °C: (1) 4-nitrothiophenoxide, (2) 4-bromothiophenoxide, (3) 4-chlorothiophenoxide, (4) thiophenoxide, (5) 4-methylthiophenoxide, and (6) 4-methoxythiophenoxide. $E_{1/2} = -0.08 + 0.88E_{ox}$; $R = 0.995$.

of the small effects of the particular remote (para) substituents used in this plot. For phenols, Bordwell[41] has obtained a good linear correlation for a plot of $E_{ox}[A^-]$ vs pK_{HA}s of meta-substituted phenols. The deviation of the 4-substituted phenols from this plot has been attributed to the destabilization of their radicals by strong electron withdrawal and stabilization by electron delocalization. A similar deviation was observed by Bordwell[42] for the 4-NO_2 and 4-MeO substituents in the corresponding plot involving thiophenoxides. Hence, caution should be exercised in interpreting our results for a small sample of 4-substituted thiophenoxides. Tables II–VI present the heats of heterolysis and homolysis, free energies of electron transfer, and other related properties for the 50 combinations of the nine carbenium ions with the four thiophenoxides.

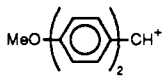
(41) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1735.
(42) Bordwell, F. G.; Cheng, J.-P. Unpublished results.

Table IV. Heats of Heterolysis and Homolysis, Free Energies of Electron Transfer (kcal/mol), and CRPs for Reactions of Triphenylcyclopropenylium and Tropylium Ions with Thiophenoxides in Sulfolane/3-Methylsulfolane (5%) at 25 °C

	 triphenylcyclopropenylium[a]			triopylium[b]		
parent thiophenol	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
4-nitrothiophenol	14.44 ± 0.11	29.72 ± 0.12	44.16 ± 0.16	12.95 ± 0.22	14.00 ± 0.12	26.95 ± 0.25
4-bromothiophenol	17.80 ± 0.14	23.61 ± 0.10	41.41 ± 0.17	17.85 ± 0.25	7.89 ± 0.10	25.74 ± 0.27
4-chlorothiophenol	18.09 ± 0.15	21.31 ± 0.21	39.40 ± 0.26	18.38 ± 0.27	5.58 ± 0.21	23.96 ± 0.34
thiophenol	20.14 ± 0.44	20.13 ± 0.12	40.27 ± 0.46	20.17 ± 0.11	4.40 ± 0.12	24.57 ± 0.16
4-methylthiophenol	20.75 ± 0.38	18.66 ± 0.12	39.38 ± 0.40	20.75 ± 0.24	2.93 ± 0.12	23.68 ± 0.27
4-methoxythiophenol	21.90 ± 0.33	17.62 ± 0.10	39.52 ± 0.34	21.61 ± 0.25	1.89 ± 0.10	23.56 ± 0.27

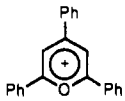
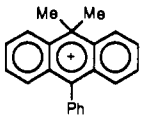
[a] pK_{R^+} = 3.1, CRP = 25.8, $E_{1/2}(C^+)$ = −1.30 ± 0.003 V. [b] pK_{R^+} = 4.7, CRP = 7.90, $E_{1/2}(C^+)$ = −0.622 ± 0.002 V.

Table V. Heats of Heterolysis and Homolysis, Free Energies of Electron Transfer (kcal/mol), and CRPs for Reactions of Perinaphthenium and 4,4′-Dimethoxydiphenylmethyl Cations with Thiophenoxides in Sulfolane/3-Methylsulfolane (5%) at 25 °C

	perinaphthenium[a]			 4,4′-dimethoxydiphenylmethyl[b]		
parent thiophenol	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
4-nitrothiophenol	16.19 ± 0.64			19.09 ± 0.67	10.03 ± 0.12	29.12 ± 0.68
4-bromothiophenol	18.50 ± 0.51	−6.16 ± 0.10	12.34 ± 0.52	23.50 ± 0.59	3.92 ± 0.10	27.42 ± 0.60
4-chlorothiophenol	20.37 ± 0.44	−8.46 ± 0.21	11.91 ± 0.49	23.88 ± 0.68	1.61 ± 0.21	25.49 ± 0.71
thiophenol	22.42 ± 0.60	−9.64 ± 0.12	12.78 ± 0.61	26.47 ± 1.22	0.44 ± 0.12	26.91 ± 1.23
4-methylthiophenol	22.98 ± 0.53	−11.11 ± 0.20	11.87 ± 0.54	27.90 ± 0.65	−1.04 ± 0.12	26.86 ± 0.66
4-methoxythiophenol	23.80 ± 0.48	−12.15 ± 0.19	11.65 ± 0.49	29.24 ± 0.47	−2.08 ± 0.10	27.16 ± 0.48

[a] pK_{R^+} = unknown, $E_{1/2}(C^+)$ = −0.013 ± 0.002 V. [b] pK_{R^+} = −5.65, CRP = 18.1, $E_{1/2}(C^+)$ = −0.450 ± 0.002 V.

Table VI. Heats of Heterolysis and Homolysis, Free Energies of Electron Transfer (kcal/mol), and CRPs for Reactions of Triphenylpyrylium and 9,9′-Dimethyl-10-phenyl-9,10-dihydroanthracenium Ions with Thiophenoxides in Sulfolane/3-Methylsulfolane (5%) at 25 °C

	 triphenylpyrylium[a]			 9,9-dimethyl-10-phenyl-9,10-dihydroanthracenium[b]		
parent thiophenol	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
4-nitrothiophenol				21.60 ± 0.60	2.72 ± 0.12	24.32 ± 0.61
4-bromothiophenol				24.75 ± 0.53	−3.39 ± 0.10	21.36 ± 0.54
4-chlorothiophenol				25.32 ± 0.51	−5.70 ± 0.21	19.62 ± 0.55
thiophenol	9.05 ± 0.12	7.82 ± 0.20	16.87 ± 0.23	27.08 ± 0.43	−6.87 ± 0.12	20.21 ± 0.45
4-methylthiophenol	10.45 ± 0.44	6.34 ± 0.20	16.79 ± 0.46	28.85 ± 0.42	−8.35 ± 0.12	20.50 ± 0.44
4-methoxythiophenol	11.47 ± 0.63	5.30 ± 0.19	16.77 ± 0.66	30.24 ± 0.44	−9.39 ± 0.10	20.85 ± 0.45

[a] pK_{R^+} = unknown, $E_{1/2}(C^+)$ = −0.770 ± 0.007 V. [b] pK_{R^+} = −5.49, CRP = 10.6, $E_{1/2}(C^+)$ = −0.133 ± 0.002 V.

Table VII. Heats of Heterolysis and Homolysis of Neutral Compounds and Heats of Cleavage of Radical Cations Derived from Tropylium[a] Thiophenoxides

compound	ΔH_{het}(CX) (kcal/mol)	ΔG_{ET} (kcal/mol)	ΔH_{homo} (kcal/mol)	$E_{1/2}(X^-)$ (V)	E_{ox}(CX) (V)	$\Delta H_{cleav}(CX^{\bullet+})$ (kcal/mol)
O_2N–C_6H_4–SC_7H_7	12.95 ± 0.22	14.00 ± 0.12	26.95 ± 0.25	−0.015 ± 0.005	1.166 ± 0.006	−14.3
Br–C_6H_4–SC_7H_7	17.85 ± 0.25	7.89 ± 0.10	25.74 ± 0.27	−0.280 ± 0.004	1.278 ± 0.013	−18.1
Cl–C_6H_4–SC_7H_7	18.38 ± 0.27	5.58 ± 0.21	23.96 ± 0.34	−0.380 ± 0.009	1.470 ± 0.005	−24.3
H–C_6H_4–SC_7H_7	20.17 ± 0.11	4.40 ± 0.12	24.57 ± 0.16	−0.431 ± 0.005	1.393 ± 0.007	−21.9
Me–C_6H_4–SC_7H_7	20.75 ± 0.24	2.93 ± 0.12	23.68 ± 0.27	−0.495 ± 0.005	1.480 ± 0.008	−24.8
MeO–C_6H_4–SC_7H_7	21.61 ± 0.25	1.89 ± 0.10	23.50 ± 0.27	−0.540 ± 0.004	1.472 ± 0.005	−24.8

[a] pK_{R^+} = 4.70, $E_{red}(C^+)$ = −0.622 ± 0.002 V. [b] The maximum error involved in these measurements is ca. 2.0 kcal/mol.

Table VIII. Heats of Heterolysis and Homolysis of Neutral Compounds and Heats of Cleavage of Radical Cations Derived from Triphenylcyclopropenylium[a] Thiophenoxides

compound	ΔH_{het}(CX) (kcal/mol)	ΔG_{ET} (kcal/mol)	ΔH_{homo} (kcal/mol)	$E_{1/2}(X^-)$ (V)	E_{ox}(CX) (V)	$\Delta H_{cleav}(CX^{\bullet+})^b$ (kcal/mol)
O_2N—⬡—S-TPCP	14.44 ± 0.11	29.72 ± 0.12	44.16 ± 0.16	−0.015 ± 0.005	1.229 ± 0.017	−14.3
Br—⬡—S-TPCP	17.80 ± 0.14	23.61 ± 0.10	41.41 ± 0.17	−0.28 ± 0.004	1.244 ± 0.010	−17.3
Cl—⬡—S-TPCP	18.09 ± 0.15	21.31 ± 0.21	39.40 ± 0.26	−0.380 ± 0.009	1.248 ± 0.015	−19.5
H—⬡—S-TPCP	20.14 ± 0.44	20.13 ± 0.12	40.27 ± 0.46	−0.431 ± 0.005	1.250 ± 0.012	−18.6
Me—⬡—S-TPCP	20.75 ± 0.38	18.66 ± 0.12	39.38 ± 0.40	−0.495 ± 0.005	1.256 ± 0.014	−19.6
MeO—⬡—S-TPCP	21.90 ± 0.33	17.62 ± 0.10	39.52 ± 0.34	−0.540 ± 0.004	1.261 ± 0.013	−19.6

[a] pK_{R^+} = 3.10, $E_{red}(C^+)$ = −1.304 ± 0.003 V. [b] The maximum error involved in these measurements is ca. 2.0 kcal/mol.

Table IX. Heats of Heterolysis and Homolysis of Neutral Compounds and Heats of Cleavage of Radical Cations Derived from 9-Phenylxanthylium[a] Thiophenoxides

compound	ΔH_{het}(CX) (kcal/mol)	ΔG_{ET} (kcal/mol)	ΔH_{homo} (kcal/mol)	$E_{1/2}(X^-)$ (V)	E_{ox}(CX) (V)	$\Delta H_{cleav}(CX^{\bullet+})^b$ (kcal/mol)
O_2N—⬡—S-9-PhXan	18.33 ± 0.20	7.77 ± 0.20	26.10 ± 0.28	−0.015 ± 0.005	1.229 ± 0.009	−10.4
Br—⬡—S-9-PhXan	23.05 ± 0.32	1.66 ± 0.19	24.71 ± 0.37	−0.280 ± 0.004	1.286 ± 0.020	−13.1
Cl—⬡—S-9-PhXan	24.36 ± 0.42	−0.65 ± 0.26	23.71 ± 0.49	−0.380 ± 0.009	1.310 ± 0.015	−14.6
H—⬡—S-9-PhXan	26.11 ± 0.35	−1.82 ± 0.20	24.29 ± 0.40	−0.431 ± 0.005	1.292 ± 0.010	−13.6
Me—⬡—S-9-PhXan	26.94 ± 0.19	−3.30 ± 0.20	23.64 ± 0.28	−0.495 ± 0.005	1.314 ± 0.012	−14.8
MeO—⬡—S-9-PhXan	27.85 ± 0.18	−4.34 ± 0.19	23.51 ± 0.26	−0.540 ± 0.004	1.316 ± 0.020	−15.0

[a] pK_{R^+} = 1.10, $E_{red}(C^+)$ = −0.352 ± 0.007 V. [b] The maximum error involved in these measurements is ca. 2.0 kcal/mol.

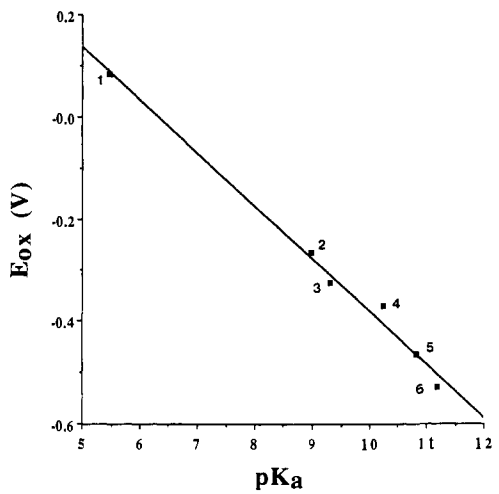


Figure 4. Plot of reversible oxidation potential ($E_{1/2}$) of the thiophenoxides in sulfolane/3-methylsulfolane (5%) vs pK_a of the thiophenoxides in DMSO:[40] (1) 4-nitrothiophenoxide, (2) 4-bromothiophenoxide, (3) 4-chlorothiophenoxide, (4) thiophenoxide, (5) 4-methylthiophenoxide, and (6) 4-methoxythiophenoxide. $E_{1/2} = 0.49 - 0.09pK_a$; $R = 0.992$.

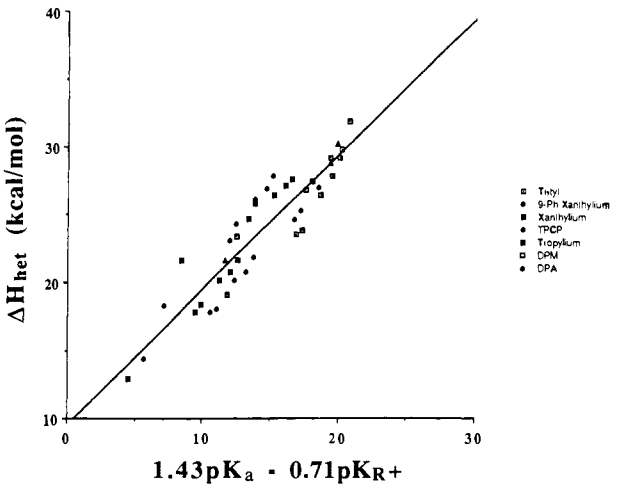


Figure 5. Correlation of heats of heterolysis of C–S bonds with ion-stabilization properties. $\Delta H_{het} = 9.54 + 1.43pK_I - 0.71pK_{R^+}$; $R = 0.917$.

Tables VII–XI present the data necessary to compare the energetics for bond cleavage for the 30 compounds formed between six thiophenoxides and five resonance-stabilized carbenium ions at 25 °C in sulfolane/5% 3-methylsulfolane. Most of the parameters are available from the data in Tables II–VI. E_{ox}[CX] is the oxidation potential of the neutral species CX leading to the corresponding radical cations. The last column shows the heats of cleavage for the radical cations derived from the neutral molecules CX. The maximum error involved in the measurements of the oxidation potentials of the radical cations and the ionic species is ±25 mV. As a consequence, the heats of cleavage of radical cations can be estimated within ca. 1.5–2 kcal/mol, a reasonably good precision for our purposes.

Discussion

In view of the different behavior of carbanions and phenoxides in the use of the pK_{R^+} acidity function for correlations of ΔH_{het}s,

Table X. Heats of Heterolysis and Homolysis of Neutral Compounds and Heats of Cleavage of Radical Cations Derived from Xanthylium[a] Thiophenoxides

compound	ΔH_{het}(CX) (kcal/mol)	ΔG_{ET} (kcal/mol)	ΔG_{homo} (kcal/mol)	$E_{1/2}(X^-)$ (V)	E_{ox}(CX) (V)	$\Delta H_{cleav}(CX^{\bullet+})^b$ (kcal/mol)
O_2N–C$_6$H$_4$–S-Xan	21.66 ± 0.33	7.66 ± 0.26	29.32 ± 0.42	−0.015 ± 0.005	1.196 ± 0.018	−6.27
Br–C$_6$H$_4$–S-Xan	24.70 ± 0.24	1.55 ± 0.25	26.25 ± 0.35	−0.280 ± 0.004	1.201 ± 0.017	−9.45
Cl–C$_6$H$_4$–S-Xan	25.87 ± 0.16	−0.76 ± 0.31	25.11 ± 0.35	−0.380 ± 0.009	1.191 ± 0.015	−10.4
H–C$_6$H$_4$–S-Xan	26.43 ± 0.38	−1.94 ± 0.26	24.49 ± 0.46	−0.431 ± 0.005	1.195 ± 0.010	−11.1
Me–C$_6$H$_4$–S-Xan	27.16 ± 0.34	−3.41 ± 0.26	23.75 ± 0.43	−0.495 ± 0.005	1.194 ± 0.014	−11.8
MeO–C$_6$H$_4$–S-Xan	27.67 ± 0.75	−4.45 ± 0.25	23.22 ± 0.51	−0.540 ± 0.004	1.194 ± 0.020	−12.3

[a] $pK_{R^+} = -0.85$, $E_{red}(C^+) = -0.347 \pm 0.010$ V. [b] The maximum error involved in these measurements is ca. 2.0 kcal/mol.

Table XI. Oxidation Potentials of Neutral Compounds and Heats of Cleavage of Radical Cations Derived from Trityl[a] Thiophenoxides

compound	E_{ox}(CX) (V)	$\Delta H_{cleav}(CX^{\bullet+})^b$ (kcal/mol)
O_2N–C$_6$H$_4$–SCPh_3	1.473 ± 0.015	−11.0
Br–C$_6$H$_4$–SCPh_3	1.477 ± 0.12	−13.7
Cl–C$_6$H$_4$–SCPh_3	1.464 ± 0.012	−15.0
H–C$_6$H$_4$–SCPh_3	1.467 ± 0.010	−14.5
Me–C$_6$H$_4$–SCPh_3	1.465 ± 0.013	−15.3
MeO–C$_6$H$_4$–SCPh_3	1.537 ± 0.015	−16.0

[a] $pK_{R^+} = -6.63$, $E_{red}(C^+) = -0.133 \pm 0.007$ V. [b] The maximum error involved in these measurements is ca. 2.0 kcal/mol.

we wanted to test its application to the carbon–sulfur bond cleavage in sulfolane. Figure 5 depicts an attempted multiple regression correlation of the ΔH_{het}s derived from Tables II–VI versus $pK_a + pK_{R^+}$ for the reactions of six thiophenoxides with seven carbenium ions (eq 8). The rather poor correlation (R =

$$\Delta H_{het} = ApK_a + BpK_{R^+} + C \quad (8)$$

0.917) of this plot compared to that of the phenoxides (R = 0.991)[32] indicates that the pK_{R^+} values for ionization of the C–O bonds of carbinols in aqueous H_2SO_4[37] are not good models for the heterolysis of carbon–sulfur bonds in sulfolane. This observation is in accordance with the predictions we made earlier.[3t] However, the correlation is vastly improved if the pK_{R^+} values are scaled to the heats of reaction of the respective carbenium ions with a standard thiophenoxide (potassium thiophenoxide), as shown in Figure 6 (R = 0.986), a method we have used previously for scaling C–C bonds.

Electrochemical Correlations. In our earlier studies,[3t,32] we correlated ΔH_{het}s versus free energies of single-electron transfer (ΔG_{ET}) from carbanions and phenoxides to carbenium ions. Since both processes involve the conversion of a neutral species (a covalent compound or a radical) to ions, fairly good correlations were found between them. Figure 7 shows the correlation of calorimetrically determined ΔH_{het}s with electrochemically determined ΔG_{ET}s for a series of thiophenoxides with trityl and tropylium ions.

Heats of Homolysis. ΔH_{het}s may be combined with ΔG_{ET}s to give ΔH_{homo}s, provided the following conditions are satisfied: (1) ΔG_{ET}s are based on reversible electrode potentials and (2) entropies of electron transfer (ΔS_{ET}) are negligible or can be calculated and

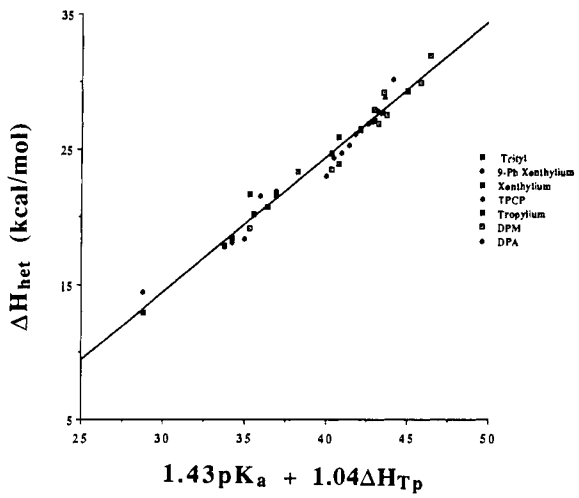


Figure 6. Correlation of heats of heterolysis of C–S bonds with modified ion-stabilization properties. $\Delta H_{het} = -15.6 + 1.43pK_a + 1.04\Delta H_{Tp}$; R = 0.986.

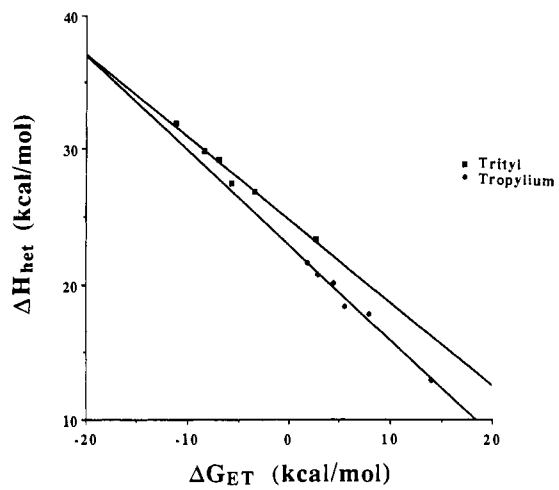


Figure 7. Comparison of heats of heterolysis of triphenylmethylium and tropylium ions with ΔG_{ET} for the thiophenoxides. For triphenylmethylium ion, $\Delta H_{het} = 24.8 - 0.61\Delta G_{ET}$; R = 0.991. For tropylium ion, $\Delta H_{het} = 22.9 - 0.70\Delta G_{ET}$; R = 0.992.

used to convert ΔG_{ET} into ΔH_{ET}.

The ΔG_{ET}s determined in this study are all based on the reversible electrode potentials measured by SHACV. In agreement with our study on the cleavage of carbon–carbon bonds,[3t] the results in Table XII indicate that ΔS_{ET} (= $d(E_{ox})/dT$) is negligible for the oxidation of these thiophenoxides. Hence we are justified

Table XII. Oxidation Potentials of Thiophenoxides (V) in Sulfolane/3-Methylsulfolane (5%) in the Temperature Range 25–60 °C

anion of	oxidation potentials (V)[a]			
	25 °C	40 °C	50 °C	60 °C
4-nitrothiophenol	+0.083	+0.079	+0.081	+0.084
4-bromothiophenol	−0.264	−0.260	−0.262	−0.260
4-chlorothiophenol	−0.326	−0.332	−0.334	−0.330
thiophenol	−0.370	−0.369	−0.375	−0.373
4-methylthiophenol	−0.465	−0.469	−0.467	−0.463
4-methoxythiophenol	−0.530	−0.534	−0.532	−0.534

[a] $E_{1/2}$ values obtained by CV. All values referenced vs ferrocene/ferrocenium redox couple using Pt working electrode, $Ag/AgNO_3$ reference electrode, and Pt auxiliary electrode. Scan rate at 25 °C is 25 mV/s; at 40–60 °C, scan rate is 100 mV/s. Standard Deviation = ±25 mV.

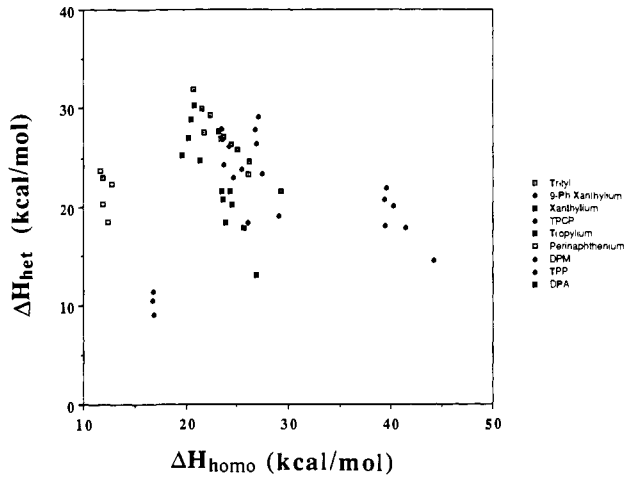


Figure 8. Plots of heats of heterolysis vs heats of homolysis for six thiophenoxides with nine carbenium ions.

in coupling the ΔH_{het} values with ΔG_{ET}s to arrive at ΔH_{homo}s. As before, a plot of ΔH_{het}s versus ΔH_{homo}s (Figure 8) is a scatter of points. This is due to the electrostatic distinction between the two processes. While ΔH_{het} involves the formation of ionic species from neutral molecules, ΔH_{homo} involves the formation of free radicals from neutral species.

A further test for the validity of these ΔH_{homo} values comes from their correlation with the bond dissociation energies (BDE) for the sulfur–hydrogen bonds in thiophenoxides derived from our $E_{1/2}$ values determined in sulfolane (corrected to the standard hydrogen electrode) and the pK_a values for the acid thiophenols measured by Bordwell's group in DMSO (eq 9).[40]

$$\mathrm{BDE} = 1.37pK_a + 23.06E_{ox}(X^-) + 55.86 \quad (9)$$

Figure 9 presents a correlation of the BDEs for thiophenols in Table II with the ΔH_{homo}s of the compounds produced by the reactions of the thiophenoxides with trityl cation ($R = 0.989$). Equally good correlations are obtained for the compounds derived from tropylium ($R = 0.988$) and xanthylium ($R = 0.986$) ions. Again, properties like heats of homolysis and bond dissociation energies, which are associated with processes involving no gain or loss of charge, correlate well with each other.

Correlation of ΔH_{homo} with Other Radical Stabilization Parameters. In previous studies, we correlated ΔH_{homo}s with two radical stabilization parameters: the acid oxidation potential (AOP) of the anion involved and the carbinol reduction potential (CRP) involving the homolytic bond dissociation energy for the carbon–oxygen bond in the carbinol precursors of the carbenium ions used to determine the pK_{R^+} values (eq 10).[31,32] Figure 10

$$\Delta H_{homo} = A(\mathrm{AOP} + \mathrm{CRP}) + B \quad (10)$$

shows the application of this equation to ΔH_{homo}s for the reactions of thiophenoxides with tropylium ion ($R = 0.990$). Similar good correlations are obtained for such plots involving the other carbenium ions.

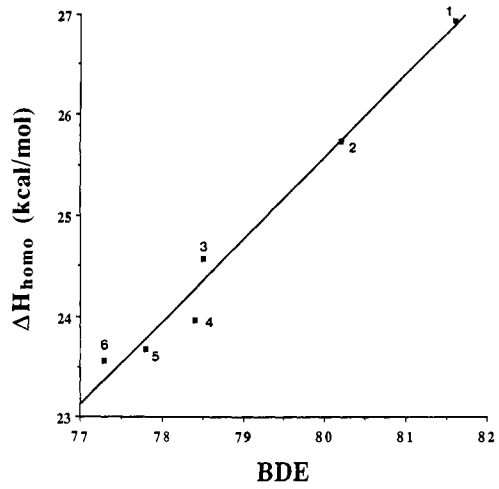


Figure 9. Plot of heats of homolysis vs bond dissociation energies for tropylium ion with thiophenoxides: (1) 4-nitrothiophenoxide, (2) 4-bromothiophenoxide, (3) thiophenoxide, (4) 4-chlorothiophenoxide, (5) 4-methylthiophenoxide, and (6) 4-methoxythiophenoxide. $\Delta H_{homo} = -40.1 + 0.82\mathrm{BDE}$; $R = 0.989$.

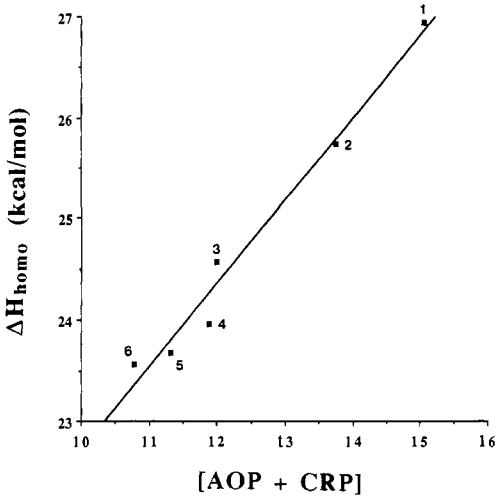


Figure 10. Plot of heats of homolysis vs [AOP + CRP] for tropylium ion with thiophenoxides: (1) 4-nitrothiophenoxide, (2) 4-bromothiophenoxide, (3) thiophenoxide, (4) 4-chlorothiophenoxide, (5) 4-methylthiophenoxide, and (6) 4-methoxythiophenoxide. $\Delta H_{homo} = -40.1 + 0.82[\mathrm{AOP} + \mathrm{CRP}]$; $R = 0.990$.

Heats of Cleavage. An examination of the $\Delta H_{cleav}^{\bullet+}$ values for the radical cations in Tables VII–XI shows a dramatic difference between the driving forces for cleaving the radical cations as compared to their neutral precursors. The highly exothermic $\Delta H_{cleav}^{\bullet+}$s of these radical cations attest to their ready decomposition into radicals and ions as soon as they are formed in solution. The corresponding radical anions are so unstable that they cannot be detected by any of the voltammetric techniques we have employed. An important driving force for the spontaneous cleavage of the radical cations is undoubtedly the relatively high stabilities of the resonance-stabilized carbenium ions formed from them.

$\Delta H_{cleav}^{\bullet+}$ values reflect the enthalpy differences between the radical cations and their cleavage products. Any rational analysis in terms of the product ions and radicals is not possible without considering the effect of structure on the stabilities of the radical cations. We can obtain some insight on this problem from the oxidation potentials of the neutral compounds if we assume that there are negligible differences in their heats of formation. A perusal of the results in Tables VI–XI clearly reveals that the trends in $E_{ox}[CX]$ are generally in agreement with the stabilities of the product carbenium ions. For example, the oxidation potentials are the lowest for the formation of the most stable car-

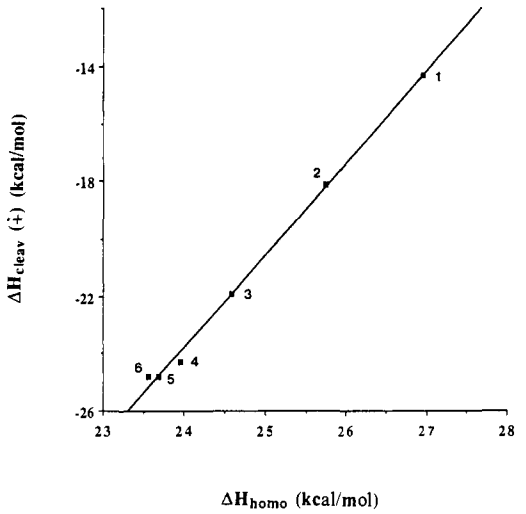


Figure 11. Plot of heats of cleavage of radical cations vs heats of homolysis for tropylium thiophenoxides: (1) 4-nitrothiophenoxide, (2) 4-bromothiophenoxide, (3) thiophenoxide, (4) 4-chlorothiophenoxide, (5) 4-methylthiophenoxide, and (6) 4-methoxythiophenoxide. $\Delta H_{cleav}^{\bullet+} = -100 + 3.20\Delta H_{homo}$; $R = 0.998$.

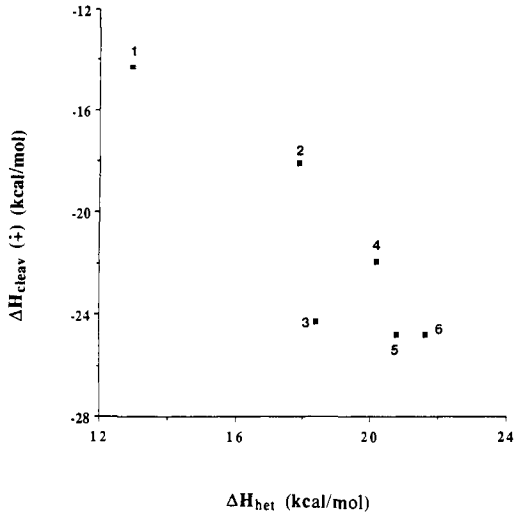


Figure 12. Plot of heats of cleavage of radical cations vs heats of heterolysis for tropylium thiophenoxides: (1) 4-nitrothiophenoxide, (2) 4-bromothiophenoxide, (3) 4-chlorothiophenoxide, (4) thiophenoxide, (5) 4-methylthiophenoxide, and (6) 4-methoxythiophenoxide.

benium ion, i.e., tropylium ion, and the largest for the formation of the least stable trityl cation. The variations in the values of E_{ox}[CX] and $\Delta H_{cleav}^{\bullet+}$ for a series of thiophenoxides are also similar for the various carbenium ions. However, no direct correlation can be obtained between the enthalpies of cleavage of the radical cations and the stabilities of the carbenium ions as represented by their pK_{R^+} values.

Relationship between $\Delta H_{cleav}^{\bullet+}$ of Radical Cations and ΔH_{het} and ΔH_{homo} of Neutral Molecules. Figures 11 and 12 show that the heats of cleavage of the radical cations correlate much better with ΔH_{homo} than with ΔH_{het} for the tropylium thiophenoxides and their radical cations. Equivalent correlations were obtained for the other four sets of compounds in Table VIII–XI. $\Delta H_{cleav}^{\bullet+}$s also correlate well with radical stabilization parameters such as AOP and CRP (Figure 13). $\Delta H_{cleav}^{\bullet+}$ values are associated with a process which involves the conversion of charged species (radical cations) into charged ions and neutral free radicals. This is electrostatically similar to homolysis where there is neither a loss nor a gain of charge. Hence, the correlation of $\Delta H_{cleav}^{\bullet+}$ with ΔH_{homo} and other similar properties is to be expected and is found.

All of the results obtained here and in our previous studies[3t,32,38] follow the general rules: (1) those properties associated with

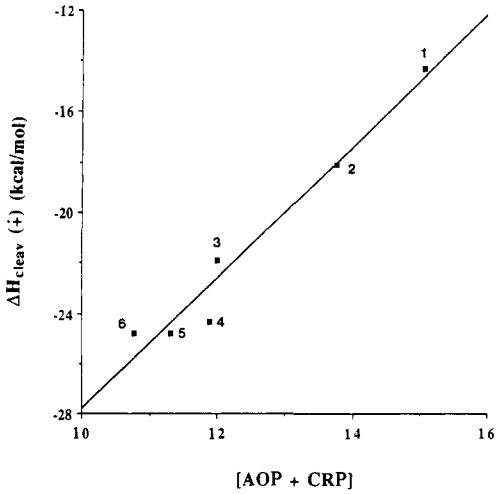


Figure 13. Plot of heats of cleavage of radical cations vs [AOP + CRP] for tropylium thiophenoxides: (1) 4-nitrothiophenoxide, (2) 4-bromothiophenoxide, (3) thiophenoxide, (4) 4-chlorothiophenoxide, (5) 4-methylthiophenoxide, and (6) 4-methoxythiophenoxide. $\Delta H_{cleav}^{\bullet+} = -53.9 + 2.61$[AOP + CRP]; $R = 0.980$.

processes which involve either a loss or a gain of charge (e.g., ΔH_{het}, pK_a, $E_{ox}X^-$ etc.) correlate with each other; (2) those properties associated with processes which do not involve a change of charge (e.g., ΔH_{homo}, $\Delta H_{cleav}^{\bullet+}$, AOP and CRP etc.) correlate with each other; and (3) there is no general correlation between the above two types of properties. However, a referee notes that in several cases there are good correlations between the ΔH_{homo}s for the neutral thio compounds reported here and the corresponding $E_{ox}[S^-]$ values and also for several E_{ox}[CS]s, so rule 3 will need to be examined further. Finally, the slopes of all correlation lines involving $\Delta H_{cleav}^{\bullet+}$s and ΔH_{homo}s are positive. This means that the effect of substitution on the thiophenoxyl radical is the same whether it is derived from the neutral molecule or its radical cation. A similar observation was made in our previous study involving the fluorenides and the carbenium ions.[38]

Conclusions

1. Oxidation potentials have been determined for six thiophenoxides in a sulfolane/5% 3-methylsulfolane solvent mixture by CV and SHACV.
2. ΔH_{het}s for 50 carbon–sulfur bonds are derived from calorimetrically measured heats of reaction of nine resonance-stabilized carbenium ions with six thiophenoxides.
3. ΔS_{ET}s for the reactions involving the thiophenoxides are found to be negligible by a study of the temperature dependence of their oxidation potentials.
4. ΔH_{homo}s are derived from ΔH_{het}s and ΔG_{ET}s by means of an appropriate thermodynamic cycle.
5. ΔH_{cleav}s have been determined for the radical cations derived from the neutral compounds formed between the series of six thiophenoxides and five resonance-stabilized carbenium ions. These enthalpies of cleavage are highly exothermic, indicating the extreme instability of the radical cations.
6. The radical anions derived from these compounds are so unstable that they cannot be detected by the voltammetric techniques used.
7. As observed before, processes which involve the loss or gain of charge (e.g., ΔH_{het}, pK_a, $E_{ox}(X^-)$) correlate with each other. Good correlations are also found for processes in which there is no change of charge (e.g., ΔH_{homo}, $\Delta H_{cleav}^{\bullet+}$). In contrast to our previous studies, there are correlations between examples of the two sets of properties for some cases reported here.
8. The results reported here are relevant to basic coal chemistry since thiophenols and related sulfur compounds form an integral part of the macromolecular structure of coal.

Acknowledgment. Support of this work was provided by the Gas Research Institute (GRI) for which we are most appreciative.