um/carbon (5 mg) was stirred under an atmosphere of hydrogen overnight. After the catalyst was filtered off, the desired product was purified on a flash column (3% methanol/methylene chloride) and obtained as a solid: IR 3454 cm^{-1} (bd, O–H), 3318 (m, N–H), 1735 (s, ester C═O); MS (Cl) *m/e* 639 ((M + 29)$^+$, 10), 611 ((M + 1)$^+$, 100), 593 ((M + 1)$^+$ – H_2O, 95); NMR (300 MHz) δ 10.34, 10.03, 10.01, 10.00, 9.99, 9.97 (4 H, a, b, g, and d meso-H), 6.32 (q, 1 H, 2a- and 4a-H of hydroxy ethyl), 4.34 (m, 4 H, 6a- and 7a-CH_2), 4.05 (m, 2 H, 2a- and 4a-CH_2), 3.66, 3.65, 3.64, 3.57, 3.56, 3.55 (overlapping s's, 18 H, 1,3,5,8-Me and 6,7-OMe), 3.25 (t, 4 H, 6b- and 7b-CH_2), 2.14 (d, 3 H, 2a- and 4a-Me of hydroxy ethyl), 1.84 (t, 3 H, 2a- and 4a-Me of ethyl).

2(4)-[1-[[(1-Oxy-2,2,5,5-tetramethylpyrrolidin-3-yl)carbonyl]oxy]ethyl]-4(2)-ethyl-6,7-bis[2-(methoxycarbonyl)ethyl]-1,3,5,8-tetramethylporphyrin (VA,B). The nitroxide derivative was prepared by the DCC coupling reaction with 3-carboxy-PROXYL and the hydroxy porphyrin. A and B isomers were separated by TLC (3‰ methanol/methylene chloride) but were not uniquely identified as to substituant position (2 or 4). *2(4)-carboxy-PROXYL-4(2)-ethylhematoporphyrin IX DME (VA)*: IR 3316, (m, N–H), 1735 (s, ester C═O) cm^{-1}; MS (Cl) *m/e* 807 ((M + 29)$^+$, 1), 779 ((M + 1)$^+$, 3), 764 ((M + 1)$^+$ – 15, 8), 593 ([M + 1]$^+$ – H_2O, 100).

Acknowledgment. This work was supported by the Office of Naval Research under ONR Contract N00014-87-K-007 and Grant N00014-89-J-1260 (N.V.B.), and ONR Contract N00014-88-K-0388 (P.S.H.). Partial support for SG was provided by the Environmental Protection Agency. Fluorescence lifetime measurements were made possible through MIT's Laser Biomedical Research Center, an NIH funded facility at the George R. Harrison Spectroscopy Laboratory. We also thank K. An for help with the lasers and data deconvolution. This is contribution No. 7348 from the Woods Hole Oceanographic Institution.

Supplementary Material Available: A listing of atomic coordinates for low-energy conformations of IA, IIA, and IIIA (8 pages). Ordering information is given on any current masthead page.

Heterolysis and Homolysis Energies for Some Carbon–Oxygen Bonds

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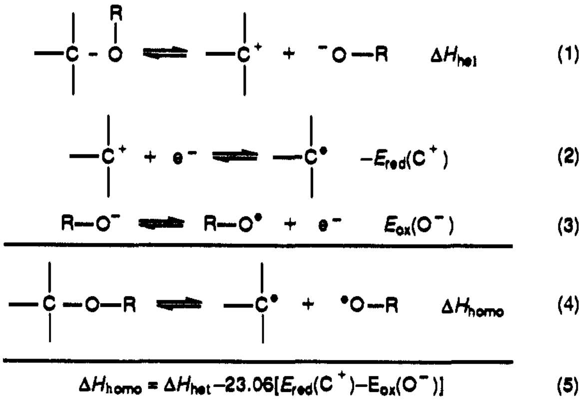
Abstract: Methods described previously for obtaining heterolysis (ΔH_{het}) and homolysis (ΔH_{homo}) enthalpies for bonds that can be cleaved to produce resonance-stabilized carbenium ions, anions, and radicals are extended to the study of carbon–oxygen bonds through the reactions of resonance-stabilized carbenium ions with substituted phenoxide ions. Titration calorimetry was used to obtain the heat of heterolysis, and the second-harmonic ac voltammetry (SHACV) method was used to obtain reversible oxidation potentials for the anions. In several cases, the electrode reactions were so fast that reversible potentials were obtained only with the greatest difficulty. Nonetheless, there is remarkably good agreement between these oxidation potentials for phenoxide ions obtained by electrochemical methods in sulfolane solution and those reported by others using entirely different techniques in different media. Such agreement provides unprecedented evidence for the soundness of the various methods used to study redox potentials of organic ions and radicals. As before, a wide variety of correlations was tested between ΔH_{het} and ΔH_{homo}. These two properties showed little correlation with each other, but ΔH_{het} gave good correlations between many properties for which neutral species are converted into ions or vice versa, such as redox potentials of both types of ions, the pK_as of the anions, or the free energies of electron transfer. In contrast to the earlier study of cleavage to carbanions and carbenium ions, the present ΔH_{het} values are predicted well by a general equation that employs the pK_{R^+} of the carbenium ion (without modification) and the pK_a of the phenol. The improvement is consistent with the fact that the cleavage of carbon–oxygen bonds of the triarylcarbinols used to establish the pK_{R^+} stability scale is a 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.

Introduction

The present paper is relevant to the general question of the formation and cleavage of carbon–oxygen bonds and to more specialized matters such as the degradation of natural and synthetic polymers. The precursor materials, such as lignin from which coals are formed, contain various types of carbon–oxygen linkages (e.g., O–CH_3).[1-6] Phenols, catechols, and methoxyphenols are present in xylem tissue from degraded wood and coalified logs.[4] Stein has shown recently that the carbon–oxygen bond is one of the first bonds to be homolyzed during depolymerization of coal.[7,8]

Scheme I



$$\Delta H_{\text{homo}} = \Delta H_{\text{het}} - 23.06[E_{\text{red}}(C^+) - E_{\text{ox}}(O^-)] \quad (5)$$

Electron-pair bonds have two possible modes of cleavage: heterolysis to form a pair of ions or homolysis to produce a pair of the corresponding radicals.[9] Since all chemical reactions occur through the making and breaking of bonds, reliable heats of

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Table I. E Values (V) for Potassium Phenoxides in Sulfolane/3-Methylsulfolane Solvent[a]

anion	E_{ox}	$E_{1/2}$	technique and conditions
4,6-dinitro-*o*-cresolate	0.651 ± 0.005	0.635 ± 0.010	SHACV, Pt electrode, 8°/98° ac amplitude 100 mV, frequency 25 Hz
4-nitrophenoxide	0.324 ± 0.004	0.255 ± 0.015	SHACV, Pt electrode, 92°/182° ac amplitude 90 mV, frequency 25 Hz
4-cyanophenoxide	0.219 ± 0.010	0.080 ± 0.010	SHACV, GC electrode, 16°/106° ac amplitude 50 mV, frequency 25 Hz
3,5-dichlorophenoxide	0.177 ± 0.010	0.109 ± 0.015	SHACV, GC electrode, 40°/130° ac amplitude 90 mV, frequency 40 Hz
4-carbomethoxyphenoxide	0.112 ± 0.010	0.064 ± 0.010	SHACV, Pt electrode, 12°/102° ac amplitude 110 mV, frequency 40 Hz
4-chlorophenoxide	−0.010 ± 0.006	−0.116 ± 0.017	SHACV, Pt electrode, 12°/102° ac amplitude 90 mV, frequency 30 Hz
4-fluorophenoxide	−0.245 ± 0.005	−0.294 ± 0.010	SHACV, GC electrode, 26°/116° ac amplitude 50 mV, frequency 25 Hz
4-*tert*-butylphenoxide	−0.366 ± 0.005	−0.406 ± 0.014	SHACV, GC electrode, 24°/114° ac amplitude 50 mV, frequency 25 Hz
4-methylphenoxide	−0.448 ± 0.015	−0.516 ± 0.016	SHACV, Pt electrode, 8°/98° ac amplitude 80 mV, frequency 25 Hz
4-methoxyphenoxide	−0.540 ± 0.015	−0.563 ± 0.014	SHACV, Pt electrode, 8°/98° ac amplitude 60 mV, frequency 25 Hz
4-bromophenoxide	−0.181 ± 0.009	−0.287 ± 0.015	SHACV, Pt electrode, 6°/96° ac amplitude 140 mV, frequency 25 Hz
phenoxide	−0.200 ± 0.005	−0.270 ± 0.010	SHACV, Pt electrode, 8°/98° ac amplitude 80 mV, frequency 25 Hz
4-acetoxyphenoxide	−0.086 ± 0.015	−0.158 ± 0.014	SHACV, Pt electrode, 6°/96° ac amplitude 100 mV, frequency 25 Hz
4-iodophenoxide	−0.167 ± 0.014	−0.193 ± 0.007	SHACV, Pt electrode, 8°/98° ac amplitude 100 mV, frequency 25 Hz

[a] All E_{ox} values obtained by CV at a scan rate of 25 mV/s under an Ar blanket. 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 5–7 mM in anion concentration. All values obtained at 25 °C using Ag/AgNO$_3$ reference electrode and Pt wire auxiliary electrode. Counterion is K$^+$. Error for scan rates ranging from 25 to 100 mV/s = ±25 mV.

heterolysis (ΔH_{het}) and homolysis (ΔH_{homo}) should be primary data for predicting chemical reactivity. However, considering the fundamental importance of bond energetics to the wide range of bonding situations encountered in organic chemistry, there is a relative paucity of reliable quantitative data.[10–39] This serious information gap is caused primarily by the high reactivity of the ions and radicals that are produced by bond cleavage. Such highly reactive intermediates engage swiftly in exothermic secondary processes whose heats of reaction are difficult to separate from the initial bond cleavage energies. If, however, the primary products are stabilized by resonance, it is possible to arrive at ΔH_{het}s directly by determining the calorimetric heats of reaction for coordination of carbenium ions with anions in an appropriate solvent in which both types of species can be handled at high dilution at a convenient temperature. In earlier publications,[40–45] we have reported the application of this method to nearly 200 combinations of anions and carbenium ions. Sulfolane (tetramethylene sulfone) has proved to be an appropriate solvent with a high dielectric constant and remarkable resistance to attack by both carbenium ions and carbanions.[46,47] In order to lower its

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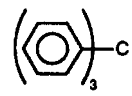
Table II. Heats of Heterolysis and Homolysis, AOPs, CRP, and Free Energies of Electron Transfer (kcal/mol) of Trityl Cation with Phenoxides in Sulfolane/3-Methylsulfolane (5%) at 25 °C



trityl[a]

parent phenol	pK_a[b]	$E_{1/2}$[c] (V)	AOP[d]	ΔH_{het}[e]	ΔG_{ET}	ΔH_{homo}[f]
4,6-dinitro-*o*-cresol	4.59	0.635 ± 0.010	20.93	21.10 ± 1.10	17.71 ± 0.28	37.82 ± 1.14
p-nitrophenol	10.78	0.255 ± 0.015	20.65	30.99 ± 0.40	8.95 ± 0.38	39.94 ± 0.55
p-cyanophenol	13.20	0.080 ± 0.010	19.93	34.72 ± 0.68	4.91 ± 0.28	39.63 ± 0.74
3,5-dichlorophenol	13.56	0.109 ± 0.010	21.09	34.17 ± 1.20	5.58 ± 0.28	39.75 ± 1.23
p-carbomethoxyphenol	14.32	0.064 ± 0.010	21.09	35.59 ± 3.05	4.54 ± 0.28	40.13 ± 3.06
p-chlorophenol	16.75	−0.116 ± 0.017	20.27	39.31 ± 1.50	0.39 ± 0.42	39.70 ± 1.56
p-fluorophenol	18.10	−0.294 ± 0.010	18.02	38.29 ± 0.71	−3.71 ± 0.28	34.58 ± 0.76
p-*tert*-butylphenol	19.05	−0.406 ± 0.014	16.74	40.59 ± 0.59	−6.30 ± 0.36	34.29 ± 0.69

[a] $pK_{R^+} = -6.63$, CRP = 12.2. [b] pK_as measured by Bordwell and his co-workers in DMSO. [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 with $\Delta H_{het} = -\Delta H_{rxn}$ (kcal/mol). [f] Calculated with the equation $\Delta H_{homo} = \Delta H_{het} + \Delta G_{ET}$ where $\Delta G_{ET} = 23.06[E_{1/2}(O^-) - E_{1/2}(C^+)]$.

freezing point below the working temperature of 25 °C in the calorimeter, 5 vol % of 3-methylsulfolane is added. ΔH_{het}s obtained in this way can be converted into the corresponding ΔH_{homo}s by means of the following cycle with the electrochemically determined redox potentials of the cation and anion (Scheme I).

This approach is an exact analogue to that reported by Brauman,[48,49] Arnold,[50] Friedrich,[51] and Bordwell[52] for determination of dissociation energies of bonds from various atoms to hydrogen through their pK_as and anion oxidation potentials. In the above case, carbenium ions take the place of the proton so that bond dissociation energies (BDEs) for a variety of C–O bonds may be obtained rather than just a series of H–O bonds.

Recently, we reported the application of these procedures to 70 carbon–carbon bonds and demonstrated that although ΔH_{het}s and ΔH_{homo}s were not correlated with each other, each property gave very good correlations with a variety of others depending only on whether a change of charge occurred in the process.[44] Thus, ΔH_{het} correlated well with redox potentials, single-electron-transfer energies, and the pK_as of the carbon acids from which the carbanions were generated.

However, whenever pK_{R^+} values were used[53] to represent the stabilization energies for the carbenium ions, much poorer correlations were obtained than if quantum mechanical delocalization energies or appropriately scaled calorimetric energies based on the reactions of the carbenium ions with a single standard carbanion (9-carbomethoxyfluorenide) were used.[44] The relatively poor performance of pK_{R^+} as a carbenium ion stability parameter was attributed to the fact that it was derived from the free energies of ionization in aqueous sulfuric acid solutions of the carbinol precursors of the carbenium ions. It was argued that the cleavage of carbon–oxygen bonds in aqueous acid was a poor model for the cleavage of carbon–carbon bonds in sulfolane/3-methylsulfolane solution.

In order to test this proposal and also to extend our methodology to the determination of heterolytic and homolytic energies for cleavage of carbon–oxygen bonds, reactions of the previously studied carbenium ions with a series of substituted phenoxide ions were examined with the same techniques and conditions as those employed previously for carbon–carbon bonds. As will be shown, ΔH_{het}s for the carbon–oxygen bonds reported here do in fact correlate better with pK_{R^+} than the ΔH_{het}s determined for carbon–carbon bonds.

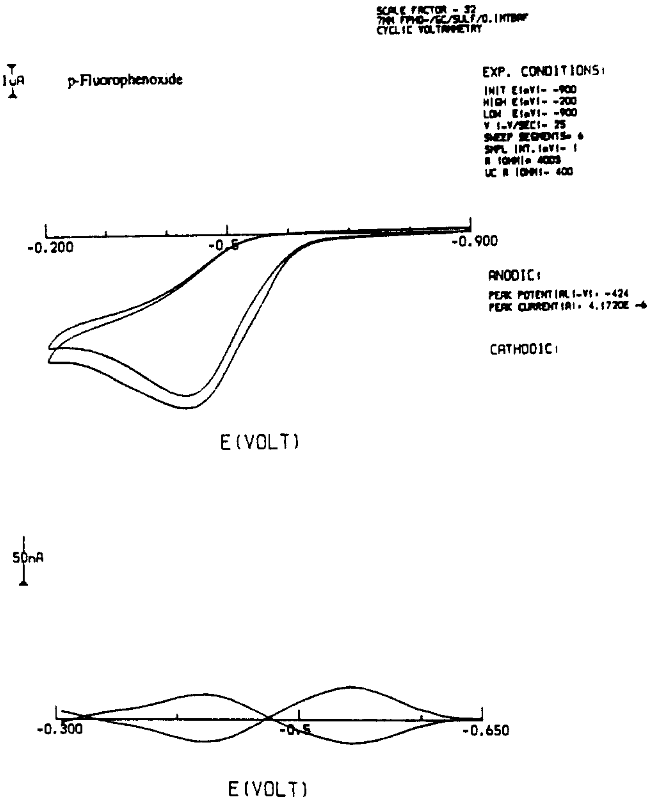


Figure 1. Irreversible cyclic voltammogram (CV, top) and reversible second-harmonic ac voltammogram (SHACV, bottom) for the oxidation of 4-fluorophenoxide in sulfolane/3-methylsulfolane (5%).

Experimental Methods

The calorimetric and electrochemical techniques were the same as those described previously.[44,54] The reduction potentials for the cations have also been reported.[44] Figure 1 compares an ordinary cyclic voltammagram to that obtained by the second-harmonic ac voltammetry (SHACV) technique for a typical phenoxide ion. Derived values for E_{ox} and $E_{1/2}$ are listed in Table I for 14 phenoxide ions along with the optimum conditions for obtaining them.

In view of the difficulty in obtaining reliable oxidation potentials for the phenoxide ions, two completely independent studies were done by N.G.H. and S.V. Although excellent agreement was found in most cases, sharp discrepancies were observed for 2,4-dinitro-*o*-cresolate, 4-cyanophenoxide, and 4-*tert*-butylphenoxide ions. Naturally, we have used what we consider to be the better data, which also give the best fits to corre-

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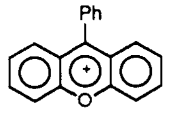
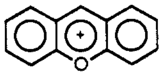
Table III. Heats of Heterolysis and Homolysis, CRP's, and Free Energies of Electron Transfer (kcal/mol) of 9-Phenylxanthylium and Xanthylium Cations with Phenoxides in Sulfolane/3-Methylsulfolane (5%) at 25 °C

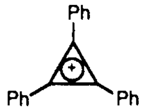




parent phenol	9-phenylxanthylium[a]			xanthylium[b]		
	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
4,6-dinitro-*o*-cresol						
p-nitrophenol	15.04 ± 0.11	13.99 ± 0.38	29.03 ± 0.40	19.65 ± 0.26	13.88 ± 0.42	33.53 ± 0.49
p-cyanophenol	17.32 ± 0.56	9.96 ± 0.28	27.28 ± 0.63	23.38 ± 0.36	9.85 ± 0.33	33.23 ± 0.49
3,5-dichlorophenol	18.23 ± 0.33	10.63 ± 0.38	28.86 ± 0.50	24.66 ± 0.61	10.51 ± 0.42	35.17 ± 0.74
p-carbomethoxyphenol	18.25 ± 0.09	9.59 ± 0.28	27.84 ± 0.29	24.54 ± 0.34	9.48 ± 0.33	34.02 ± 0.47
p-chlorophenol	22.06 ± 0.09	5.44 ± 0.42	27.50 ± 0.43	27.93 ± 1.42	5.33 ± 0.45	33.26 ± 1.49
p-fluorophenol	23.85 ± 0.16	1.34 ± 0.28	25.19 ± 0.32	29.67 ± 0.29	1.22 ± 0.33	30.89 ± 0.44
p-*tert*-butylphenol	26.27 ± 0.87	−1.24 ± 0.36	25.03 ± 0.94	32.84 ± 0.35	−1.36 ± 0.40	31.48 ± 0.53

[a] pK_{R^+} = 1.1, CRP = 6.84. [b] pK_{R^+} = −0.85, CRP = 9.15.

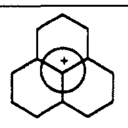
Table IV. Heats of Heterolysis and Homolysis, CRP's, and Free Energies of Electron Transfer (kcal/mol) of Triphenylcyclopropenylium and Tropylium Cations with Phenoxides in Sulfolane/3-Methylsulfolane (5%) at 25 °C

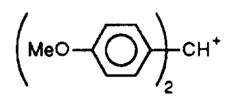


parent phenol	triphenylcyclopropenylium[a]			tropylium[b]		
	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
4,6-dinitro-*o*-cresol						
p-nitrophenol	11.53 ± 0.85	35.95 ± 0.49	47.48 ± 0.98	10.64 ± 0.66	20.22 ± 0.35	30.86 ± 0.75
p-cyanophenol	14.36 ± 0.28	31.92 ± 0.42	46.28 ± 0.50	13.25 ± 0.34	16.19 ± 0.23	29.44 ± 0.41
3,5-dichlorophenol	13.95 ± 0.11	32.58 ± 0.49	46.53 ± 0.50			
p-carbomethoxyphenol	16.31 ± 0.33	31.55 ± 0.42	47.86 ± 0.53	14.21 ± 0.38	15.81 ± 0.23	30.02 ± 0.44
p-chlorophenol	18.86 ± 0.55	27.40 ± 0.52	46.26 ± 0.76	16.98 ± 0.49	11.67 ± 0.39	28.65 ± 0.63
p-fluorophenol	20.12 ± 0.61	23.29 ± 0.42	43.41 ± 0.74	18.19 ± 0.29	7.56 ± 0.23	25.75 ± 0.37
p-*tert*-butylphenol	21.54 ± 1.54	20.71 ± 0.47	42.25 ± 1.61	20.25 ± 0.35	4.98 ± 0.32	25.25 ± 0.47

[a] pK_{R^+} = 3.1, CRP = 25.8. [b] pK_{R^+} = 4.7, CRP = 7.90.

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





parent phenol	perinaphthenium[a]			4,4′-dimethoxydiphenylmethyl[b]		
	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
4,6-dinitro-*o*-cresol	17.23 ± 0.64	14.94 ± 0.24	32.17 ± 0.68	20.13 ± 0.55	25.02 ± 0.24	45.15 ± 0.60
p-nitrophenol	32.36 ± 1.46	6.18 ± 0.35	38.54 ± 1.50	31.41 ± 1.25	16.25 ± 0.35	47.66 ± 1.30
p-cyanophenol	38.77 ± 0.93	2.14 ± 0.24	40.91 ± 0.96	39.83 ± 0.56	12.22 ± 0.24	52.05 ± 0.61
3,5-dichlorophenol						
p-carbomethoxyphenol	36.36 ± 0.78	1.78 ± 0.24	38.14 ± 0.82	41.53 ± 1.86	11.85 ± 0.24	53.38 ± 1.88
p-chlorophenol	41.88 ± 1.38	−2.38 ± 0.39	39.50 ± 1.43	44.23 ± 0.40	7.70 ± 0.39	51.93 ± 0.56
p-fluorophenol	49.34 ± 0.67	−6.48 ± 0.24	42.86 ± 0.71	45.50 ± 0.42	3.60 ± 0.24	49.10 ± 0.48
p-*tert*-butylphenol	54.40 ± 2.12	−9.06 ± 0.33	45.34 ± 2.15	48.22 ± 1.35	1.01 ± 0.33	49.23 ± 1.39

[a] pK_{R^+} = unknown. [b] pK_{R^+} = −5.65, CRP = 18.1.

lation equations and agree best with values from a recent pulse radiolysis study for the same radicals.[55] However, we acknowledge the unusual difficulty in obtaining these data, which makes their agreement with other independent data (infra vide) especially significant.

Results

The $E_{1/2}$ numbers in Table I differ by a nearly constant 56 mV (more negative) from the irreversible E_{ox} values, and Figure 2 demonstrates that $E_{1/2}$ varies linearly with E_{ox} with a slope of 0.9943. The experimental error propagated by our thermodynamic cycle for obtaining ΔH_{homo} from ΔH_{het}, E_{ox}, and E_{red} can be derived without significant error by interchanging E_{ox} and $E_{1/2}$. Tables II–VI present the heats of heterolysis and homolysis, free energies of electron transfer, and other related properties for 60 combinations of the nine carbenium ions with the eight phenoxide ions.

Discussion

An important motive for this research was to test the use of the pK_{R^+} acidity function in correlations of ΔH_{het}s for the 60 carbon–oxygen bonds reported here in contrast to those previously published for carbon–carbon bonds.[44] Specifically, we had demonstrated that there was a fair general correlation (R = 0.968) by eq 6 for 71 ΔH_{het}s derived from heats of reaction for a variety

$$\Delta H_{het} = ApK_a + BpK_{R^+} + C \qquad (6)$$

of carbanions with the same carbenium ions used in the present report by use of the pK_a of the carbon acid in DMSO[56] and the pK_{R^+} of the carbinol precursor to the carbenium ion in aqueous

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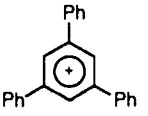
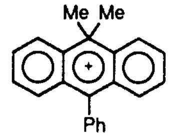
[55] Lind, J.; Shen, X.; Eriksen, T. E.; Merenyi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479.

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





parent phenol	triphenylpyrylium[a]			9,9-dimethyl-10-phenyl-9,10-dihydroanthracenium[b]		
	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
4,6-dinitro-*o*-cresol				21.40 ± 0.35	17.71 ± 0.24	39.11 ± 0.42
4-nitrophenol				28.53 ± 1.05	8.95 ± 0.35	37.48 ± 1.11
p-cyanophenol				33.48 ± 0.32	4.91 ± 0.24	38.39 ± 0.40
3,5-dichlorophenol						
p-carbomethoxyphenol	7.67 ± 0.42	19.23 ± 0.28	26.90 ± 0.50	32.39 ± 0.47	4.54 ± 0.24	36.93 ± 0.53
p-chlorophenol	9.21 ± 0.22	15.08 ± 0.42	24.29 ± 0.47	35.75 ± 0.46	0.40 ± 0.39	36.15 ± 0.60
p-fluorophenol	12.86 ± 0.17	10.98 ± 0.28	23.84 ± 0.33	38.15 ± 0.62	−3.71 ± 0.24	34.44 ± 0.66
p-*tert*-butylphenol	13.57 ± 0.68	8.39 ± 0.36	21.96 ± 0.77	40.76 ± 0.94	−6.30 ± 0.33	34.46 ± 1.00

[a] pK_{R^+} = unknown. [b] $pK_{R^+} = -5.49$, CRP = 10.6.

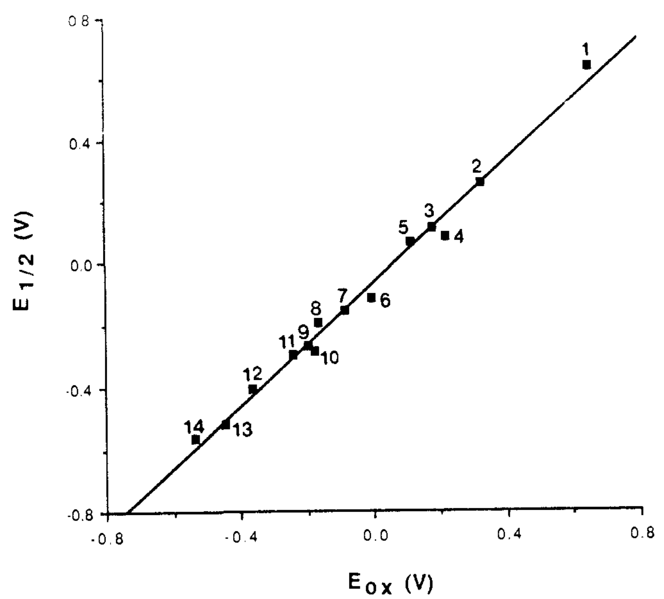


Figure 2. Plot of reversible oxidation potential ($E_{1/2}$) obtained by SHACV vs the irreversible oxidation potential (E_{ox}) obtained by CV for the phenoxides in sulfolane/3-methylsulfolane (5%): (1) 4,6-dinitro-*o*-cresolate, (2) 4-nitrophenoxide, (3) 3,5-dichlorophenoxide, (4) 4-cyanophenoxide, (5) 4-carbomethoxyphenoxide, (6) 4-chlorophenoxide, (7) 4-acetoxyphenoxide, (8) 4-iodophenoxide, (9) phenoxide, (10) 4-bromophenoxide, (11) 4-fluorophenoxide, (12) 4-*tert*-butylphenoxide, (13) 4-methylphenoxide, (14) 4-methoxyphenoxide. $E_{1/2} = -0.06 + 0.99E_{ox}$. $R = 0.9943$.

sulfuric acid solutions.[53] The overall correlation could be resolved into two separate correlation lines, one for secondary ($R = 0.975$) and one for tertiary ($R = 0.994$) carbenium ions. It was proposed that the pK_{R^+} acidity function was an inappropriate model for describing the heterolysis of carbon–carbon bonds in sulfolane because pK_{R^+} is derived from the cleavage of carbon–oxygen bonds in aqueous sulfuric acid. Support for this proposition was found in the excellent correlations that were obtained when pK_{R^+} was replaced in eq 6 by more appropriate carbenium ion stability factors.

Another test of the proposed importance of suitable models is represented here by Figure 3 in which the ΔH_{het}s derived from Tables II–VI for the reactions of eight phenoxides with six carbenium ions (two secondary, four tertiary) all fit a single line with $R = 0.992$. These results establish the point that the pK_{R^+} values for ionization of carbinols in aqueous sulfuric acid are a good model for heterolysis of carbon–oxygen bonds in other media but are inferior for the heterolysis of the corresponding carbon–carbon bonds and probably for bonds formed from carbon to other main-group elements. It is not clear why there should have been a dispersal into two lines for secondary and tertiary cations in the previous study of carbon–carbon bonds, although steric hindrance is an obvious possibility.

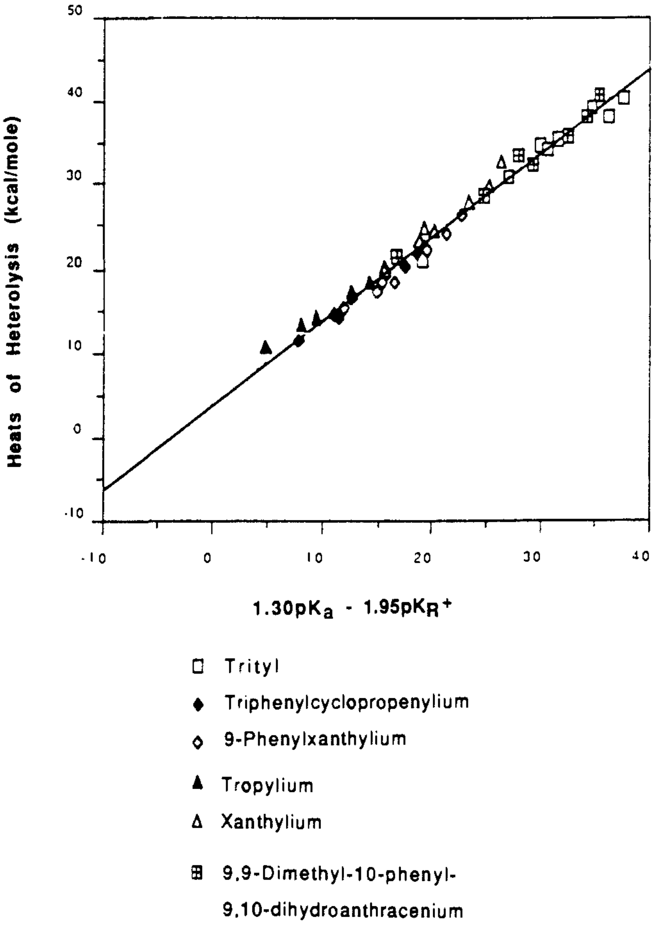


Figure 3. Correlation of heats of heterolysis for C–O bonds with ion stabilization properties. $\Delta H_{het} = 3.87 + 1.30pK_a - 1.95pK_{R^+}$. $R = 0.9920$.

Electrochemical Correlations. In view of the difficulty we encountered in determining oxidation potentials for the phenoxides, it is fortunate that a recent paper by Lind et al.[55] reports the one-electron reduction potentials for phenoxyl radicals determined from pulse radiolysis experiments in water. They also describe the difficulties of handling phenoxyl redox systems, in view of which it is assuring for both studies that the reduction potentials of the radicals in water and the oxidation potentials of the anions in sulfolane correlate fairly well ($R = 0.9715$) as shown in Figure 4.

ΔH_{het}s were correlated previously with free energies for single-electron transfer (ΔG_{ET}) from carbanions to carbenium ions.[44]

Table VII. Bond Dissociation Energies (kcal/mol) of Phenols

phenol	pK_a	$E_{1/2}$[a] (V)	AOP	$E°$[b] (V)	BDE	BDE[c]	BDE[d]	BDE[f]
4-H	18.03	−0.270 ± 0.010	18.47	0.480	91.63 ± 0.27	88.2 ± 0.5	84.0 ± 1.0[e]	63.5
4-Me	18.90	−0.516 ± 0.016	13.99	0.234	87.15 ± 0.41	86.1 ± 0.5	86.5 ± 3.1	61.6
4-F	18.10	−0.294 ± 0.010	18.02	0.456	91.17 ± 0.27	87.4 ± 0.5	86.5 ± 3.1	62.4
4-Cl	16.75	−0.116 ± 0.017	20.27	0.634	93.42 ± 0.43	87.6 ± 0.5	86.5 ± 3.1	62.4
4-NO_2	10.78	0.255 ± 0.015	20.65	1.005	93.80 ± 0.39	94.2 ± 1.4		64.6
4-OMe	19.10	−0.563 ± 0.014	13.18	0.187	86.33 ± 0.36	82.6 ± 0.5	86.5 ± 3.1	59.5
4-*t*-Bu	19.05	−0.406 ± 0.014	16.74	0.344	89.89 ± 0.36		82.1 ± 1.0[e]	
4-CN	13.20	0.080 ± 0.010	19.93	0.830	93.08 ± 0.27	92.9 ± 0.7		63.8
4-Br		−0.287 ± 0.015		0.463		88.1 ± 0.5		
4-OCOMe	14.14	−0.158 ± 0.014	15.73	0.592	88.88 ± 0.36	90.3 ± 0.5		
4-I		−0.193 ± 0.007		0.557		87.9 ± 0.5		

[a] Reversible (oxidation) potentials measured in a BAS-100A electrochemical analyzer in sulfolane/3-methylsulfolane (5%) at 25 °C by SHACV using Ag/$AgNO_3$ reference electrode, Pt working electrode, and ferrocenium/ferrocene redox couple as the internal standard. [b] Reversible (oxidation) potentials corrected to the standard hydrogen electrode by adding 0.875–0.125 = 0.750 V to the potentials for use in Bordwell's equation: BDE = 1.37pK_a + 23.06$E_{ox}(A^-)$ + 55.86. [c] Values from ref 55. [d] Values from ref 58. [e] Values from ref 59. [f] O-Me bond energies for unimolecular decomposition of substituted anisoles from ref 8.

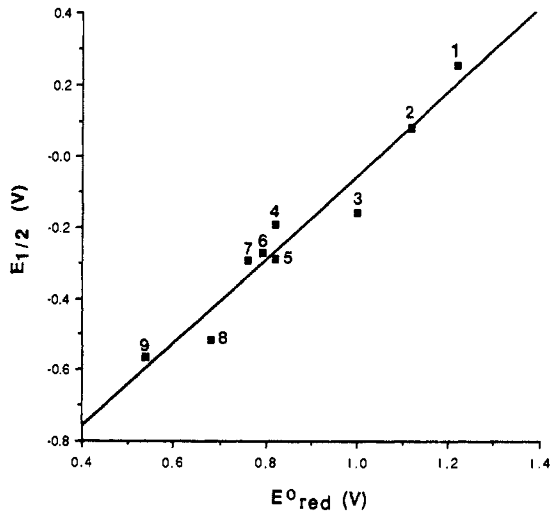
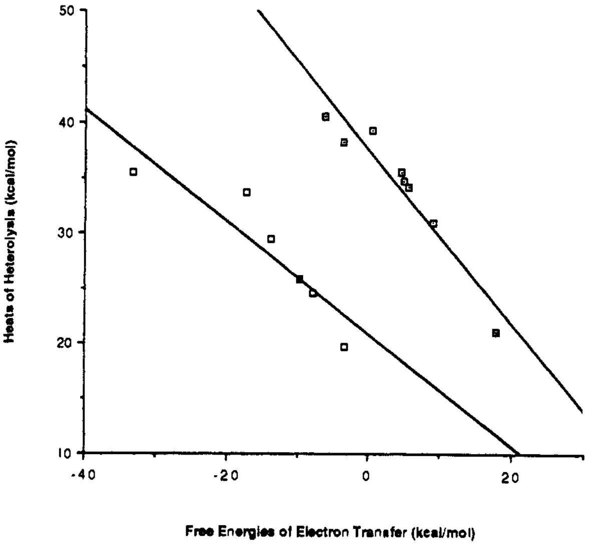


Figure 4. Plot of reversible oxidation potentials of the phenoxides obtained by SHACV in sulfolane/3-methylsulfolane (5%) vs the standard reduction potentials of phenoxy radicals[55] obtained by pulse radiolysis in water: (1) 4-nitrophenoxide, (2) 4-cyanophenoxide, (3) 4-acetoxyphenoxide, (4) 4-iodophenoxide, (5) 4-bromophenoxide, (6) phenoxide, (7) 4-fluorophenoxide, (8) 4-methylphenoxide, (9) 4-methoxyphenoxide. $E_{1/2} = -1.22 + 1.17E_{red}$. $R = 0.9715$.



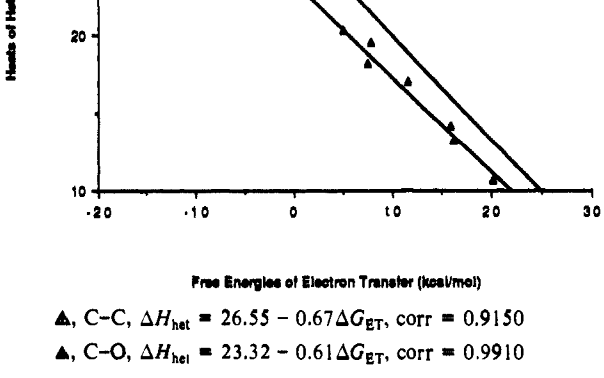
□, C-C, $\Delta H_{het} = 20.84 - 0.51\Delta G_{ET}$, corr = 0.9010

⊡, C-O, $\Delta H_{het} = 37.45 - 0.79\Delta G_{ET}$, corr = 0.9521

Figure 5. Comparison of heats of heterolysis of trityl cation with ΔG_{ET} for the fluorenides and phenoxides.

Both of these processes involve the conversion of a neutral species (a covalent compound or radical) to ions, and good correlations were found between them. Figures 5 and 6 compare the correlation of calorimetrically determined ΔH_{het}s with electrochemically determined ΔG_{ET}s for a series of carbanions and phenoxide ions reacting with the trityl and tropylium cations. In both cases, the correlations for the carbon–oxygen bonds are markedly superior to those for carbon–carbon ones. The similar slope and intercept for the carbon–oxygen and carbon–carbon series in Figure 6 are probably fortuitous since there is no obvious reason why such different types of systems should fall so close together. Figure 5 shows a clear dispersion between the two sets of data.

Heats of Homolysis. Calorimetrically determined ΔH_{het}s may be combined with electrochemically determined ΔG_{ET}s provided that the latter are based on reversible electrode potentials and that entropies of electron transfer either are negligible or can be calculated and used to convert ΔG_{ET} into ΔH_{ET}. In our previous discussion of carbon–carbon bonds, it was shown that ΔS_{ET} values were negligible within experimental error. Because of the difficulties that we encountered in obtaining oxidation potentials at a single temperature, it was not practical to obtain ΔS_{ET} from $\partial E_{ox}/\partial T$ in the present study. However, Merenyi[55] and Benson[56,57] have shown that ΔS_{ET} for the phenols is negligible. If this is also true for our results, the ΔH_{homo}s in Tables II–VI may be obtained



▲, C-C, $\Delta H_{het} = 26.55 - 0.67\Delta G_{ET}$, corr = 0.9150

▲, C-O, $\Delta H_{het} = 23.32 - 0.61\Delta G_{ET}$, corr = 0.9910

Figure 6. Comparison of heats of heterolysis of tropylium cation with ΔG_{ET} for the fluorenides and phenoxides.

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(56) O'Neal, H. E.; Benson, S. W. *Int. J. Chem. Kinet.* **1969**, *1*, 221.

(57) Benson, S. W. *Chem. Rev.* **1969**, *69*, 279.

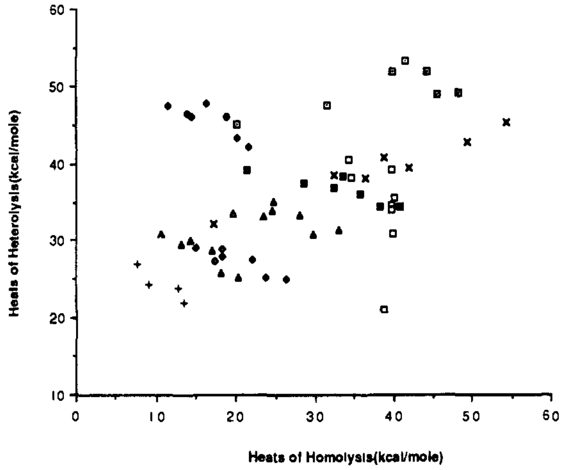

Figure 7. Plot of heats of heterolysis vs heats of homolysis for eight phenoxides with nine cations.

and compared with ΔH_{het}s. Figure 7 portrays the expected complete lack of correlation between these two fundamental properties for bond cleavage that have the basic electrostatic distinction that ΔH_{het} produces ions from neutral molecules whereas ΔH_{homo}s reflect the energies for forming neutral radicals from neutral precursors. A similar scatter diagram was found for ΔH_{het} and ΔH_{homo} of 45 carbon–carbon bonds.[44]

A further test of our data and that of Merenyi is shown in Table VII where we have calculated BDEs for homolytic cleavage of O–H bonds in the phenols and compared them with those reported by Merenyi and various other workers.[55,58,59] Our BDE values are derived from our $E_{1/2}$ values determined in sulfolane (corrected to the standard hydrogen electrode potential)[37] and pK_a values measured by Bordwell's group in DMSO.[60] Merenyi's values are derived from his pulse radiolysis reduction potentials of the radicals in aqueous solution and well-established, tabulated pK_as of the phenols in water.[61] Naturally, the best agreement is found between relative values in the various data sets. However, it is also important that there is at least a rough consensus on the absolute values derived from such different types of techniques, most of which were fraught with serious experimental difficulties. The significant differences between those of Lias et al.[58] and Merenyi and us probably reflect a combination of solvation effects and difficulties of obtaining gas-phase BDEs.

The last column in Table VII lists heats of homolysis of C–O bonds for a series of substituted anisoles examined by Suryan et al.[8] Although the trend is the same as that which we have calculated from our data and those of Bordwell, only a mediocre correlation (R = 0.8700) is obtained. In both cases, the same set of phenoxyl radicals are being formed, but from the departure of different leaving groups—the hydrogen atom or methyl radical. The poor correlation therefore must be attributed to the considerable differences in experimental methods used to obtain the data.

We have shown previously that the affinities of carbanions and phenoxide ions for protons (their pK_as) correlate well with their affinities for carbenium ions (their $-\Delta G_{\text{het}}$s or $-\Delta H_{\text{het}}$s). Correspondingly, one may consider the affinities of carbon radicals or phenoxyl radicals for hydrogen atoms compared to their affinities for carbon radical. Figure 8 presents such a correlation of the BDEs for phenols in Table VII compared to the ΔH_{homo}s of the compounds produced by reaction of the phenoxide ions with triphenylcyclopropenylium cation. Similar correlations with ΔH_{homo}s of the compounds produced from the phenoxide ions with trityl cation or tropylium ion have linear correlations with R = 0.9580 and 0.9490, respectively.

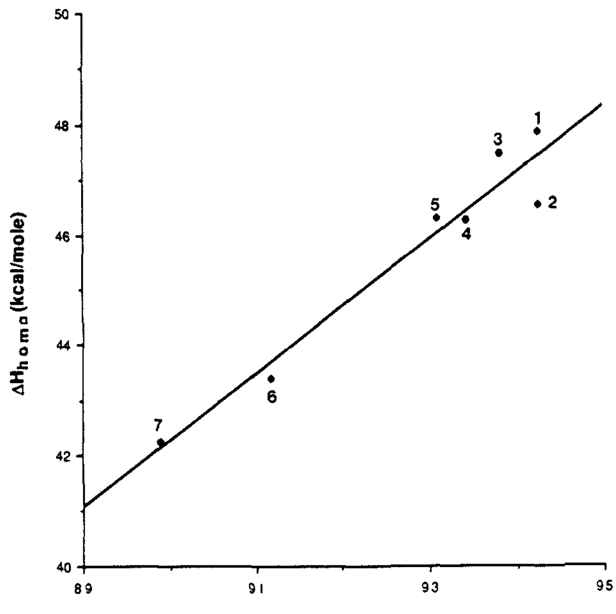

Figure 8. Plot of heats of homolysis vs bond dissociation energies for triphenylcyclopropenylium ion with the phenoxides: (1) 4-carbomethoxyphenol, (2) 3,5-dichlorophenol, (3) 4-nitrophenol, (4) 4-chlorophenol, (5) 4-cyanophenol, (6) 4-fluorophenol, (7) 4-*tert*-butylphenol. $\Delta H_{\text{homo}} = -67.1 + 1.22\text{BDE}$. R = 0.9703.

Relationship of Homogeneous to Heterogeneous Electron-Transfer Energies. The correspondence between our electrochemically determined oxidation potentials and those reported by Merenyi and others[55,62,63] is of considerable general interest in view of the wide use to which electrochemical techniques are being put for the study of single-electron transfer (SET) and other redox processes in organic chemistry. As usually discussed for mechanistic questions, SET refers to interactions between molecules, ions, or radicals in homogeneous solution. In contrast, electrochemical processes always involve ipso facto electron transfer at a solid (electrode) liquid interface. Now, electrode materials such as noble metals or carbon are some of the solid phases upon which organic molecules, and presumably radicals and ions, are especially vulnerable to strong adsorption forces, both physical and chemical, that might seriously bias the concentrations of the reactive species on the surface and the electroactive layers close to it.

Although the thermodynamics of electron transfer must be the same regardless of the pathway, one might imagine that a variety of kinetic complications could produce discrepancies between the measured homogeneous and heterogeneous processes. If so, what guarantee is there that redox potentials obtained by electrochemical methods correspond accurately to the energetics of electron transfer between isolated molecules, radicals, or ions in solution? Although this question of the relation between electrochemical equilibria and inorganic redox equilibria has had a considerable history,[64] it need not apply to organic systems where adsorption complications could be much more severe. The present study provides a clear answer for the redox behavior of these phenoxy systems, and the close correlation of our data with those of Merenyi et al. is shown in Figure 4. Of perhaps more fun-

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(58) (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1. (b) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 2222. (c) Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017.

(59) Mulder, P.; Saastad, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090 and references therein.

(60) (a) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456. (b) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463.

(61) (a) Sergeant, E. P.; Dempsey, B. *Ionisation Constants of Organic Acids in Aqueous Solution*; Pergamon Press: Oxford, 1979. (b) Professor Bordwell has pointed out that the apparent lack of solvation effects is due to large compensation effects between the pK_as and $E_{1/2}$ values.

(62) Neta, P.; Steenken, S. *Oxygen Oxy-Radicals Chem. Biol.*, [*Proc. Int. Conf. 1980*] **1981**, 83–8.

(63) Steenken, S.; Neta, P. *J. Phys. Chem.* **1979**, *83* (9), 1134 and references therein.

(64) Okamoto, K.; Takeuchi, K.; Komatsu, K.; Kubota, Y.; Ohara, R.; Arima, M.; Takahashi, K.; Waki, Y.; Shirai, S. *Tetrahedron* **1983**, *39* (23), 4011.

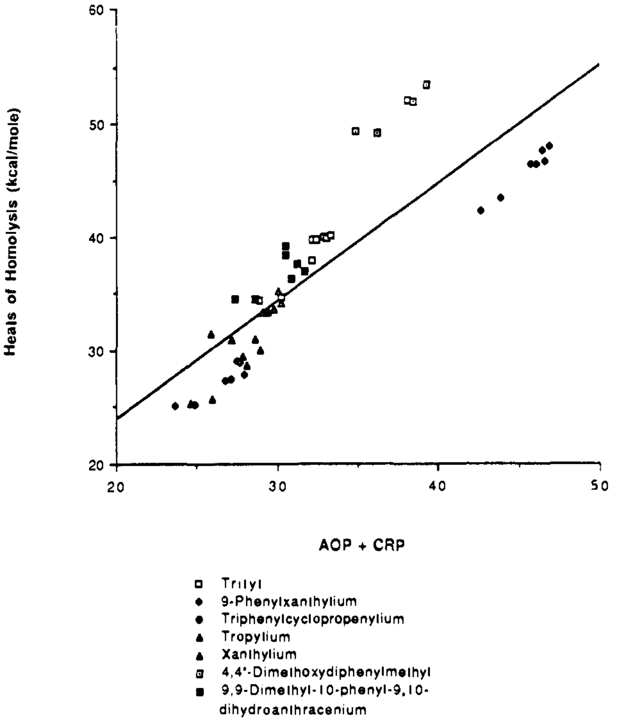

Figure 9. Plot of heats of homolysis vs AOP + CRP for seven cations with the phenoxides. $\Delta H_{homo} = 3.10 + 1.06[\text{AOP} + \text{CRP}]$. $R = 0.8410$.

damental importance is the tabulation in Table VII of BDEs derived from our data and a number of other sources. *Not only are the relative trends for the effects of substitutents on redox potentials transferable from homogeneous to heterogeneous electrode interactions, but, much more importantly, the results are probably accurate* since they agree reasonably well despite the differences in techniques.

Correlation with Other Radical Stabilization Parameters. By analogy to eq 6, which relates heats of heterolysis to radical stabilization parameters for the carbenium ion and the anion, eq 7 was proposed[44] that related ΔH_{homo} to two radical stabilization

$$\Delta H_{homo} = A(\text{AOP}) + B(\text{CRP}) + C \qquad (7)$$

properties: the bond dissociation energy for the phenols (AOP) and the carbinol reduction potential (CRP)—the homolytic bond dissociation energy for the carbon–oxygen bond in the carbinols employed for determination of pK_{R^+} values.[53] Figure 9 shows the application of this equation to ΔH_{homo}s for the carbon–oxygen compounds in Tables II–VI. As before,[44] this rather unsatisfactory correlation can be improved considerably if all of the carbinol reduction potentials are based on values scaled to the heats of reaction of the respective cations with a standard anion (*p*-carbomethoxyphenoxide) as shown in Figure 10, rather than using the pK_{R^+}.

Conclusions

1. Oxidation potentials have been determined for 14 phenoxide ions in a sulfolane/3-methylsulfolane solvent mixture and agree remarkably well with corresponding values obtained elsewhere by other techniques.

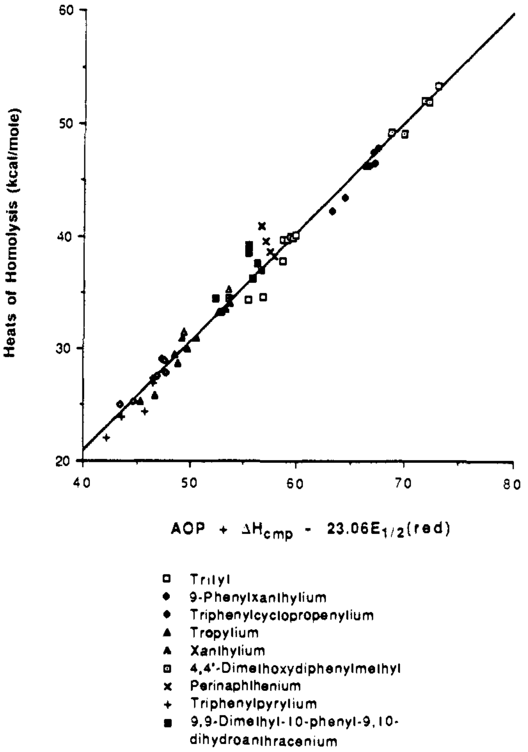

Figure 10. Plot of heats of homolysis vs AOP + $\Delta H_{cmp} - 23.06E_{1/2}$(red) for nine cations with the phenoxides. $\Delta H_{homo} = -17.9 + 0.98[\text{AOP} + \Delta H_{cmp} - 23.06E_{1/2}(\text{red})]$. $R = 0.9910$.

2. The agreement is especially important in view of the difficulty in obtaining the data and also for its demonstration that electrochemically obtained redox potentials provide an accurate assessment of the electron-transfer energies in homogeneous solution.

3. ΔH_{het}s for 61 carbon–oxygen bonds are derived from calorimetrically measured heats of reaction of 9 resonance-stabilized carbenium ions with some of the 14 phenoxide ions.

4. ΔH_{het}s correlate well with energetics of other processes for converting neutral species to charged ones, or vice versa.

5. ΔH_{homo}s are derived from ΔH_{het}s and oxidation potentials by means of an appropriate cycle.

6. ΔH_{homo}s do not correlate with ΔH_{het}s but do correlate with several other properties representing the conversion of neutral species into other neutral species.

7. ΔH_{homo}s for these carbon–oxygen bonds correlate quite well with BDEs for corresponding O–H bonds.

8. The results reported here are relevant to basic coal chemistry since phenols and other related oxygen-containing linkages such as ethers form an integral part of the basic skeleton in coal macromolecular structure.

Acknowledgment. This work was supported by the Gas Research Institute for which we are most appreciative.