Bond Cleavage Energies for Molecules and their Associated Radical Ions

Edward M. Arnett and Robert A. Flowers, II
Department of Chemistry, Duke University, Durham, North Carolina 27706, U.S.A.

1 Introduction

Most bonds between atoms are composed of electron pairs which may be broken in two ways: by division into a pair of free radicals, each of which carries one of the electrons in the previous bond, or into a pair of ions by the transfer of the electron pair to one of the fragments which becomes an anion leaving the other as a cation. The cleavage to produce radicals is referred to as *homolysis* and that to produce ions *heterolysis*. Figure 1 from Ingold's classic text 'Structure and Mechanism in Organic Chemistry' illustrates the important energy differences between the production of radicals and ions in the gas phase and in solution. In the gas phase the production of ions may be prohibitively difficult because of the enormous electrostatic attraction between cationic and anionic partners in this low dielectric medium, whereas radical formation is not limited by this problem. In solution the production of ions is also dependent on the nature of the medium and is assisted by the interaction of solvent dipoles of various types, especially hydrogen bonds.

The structure of the species undergoing bond fission also plays an important part in the choice of homolysis *vs.* heterolysis. Symmetrical molecules (*e.g.*, peroxides, RO–OR) which are lacking in a permanent dipole are predisposed toward radical formation, even in solution, whereas highly polar molecules (*e.g.*, alkyl halides, R–X) already have a head start towards heterolysis. Heterolytic cleavage may also be favoured by acid–base catalysis where the interaction of an external Lewis or Brönsted acid with the non-bonding electrons on the potential anion will help to pull it loose from the cation. Attack by an electron-rich anion on the positive end of the dipole may help to push the anion free from the cation by nucleophilic displacement, the classic substitution reaction.

The timescale for chemical transformation depends on the availability of a feasible mechanistic pathway for converting reactants into products. Many reactions occur through the formation of highly reactive intermediates (*e.g.*, free radicals, carbanions, or carbenium ions) which are formed by bond cleavage and serve as high-energy way-stations on the path to the highest energy transition state along the reaction coordinate. The activation energies required for producing these unstable species are of comparable importance to the thermodynamic ones for comparing bond strength in reactants *vs.* products.

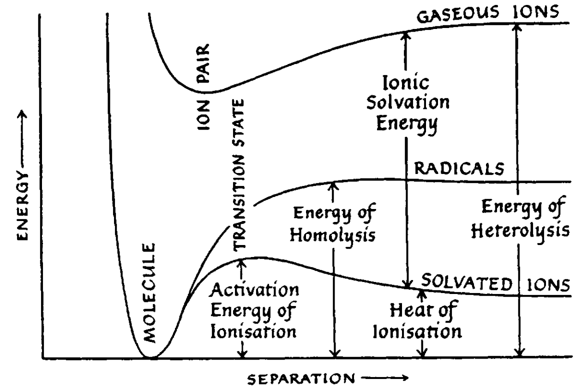


Figure 1 Schematic energy diagram for bond cleavage of covalent molecule in the gas phase and a polar solvent.
(Reprinted from C. K. Ingold, 'Structure and Mechanism in Organic Chemistry', Second Edition, 1969. Used by permission of the publisher, Cornell University Press.)

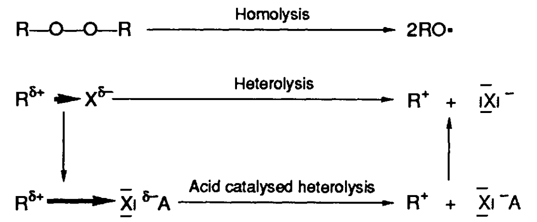
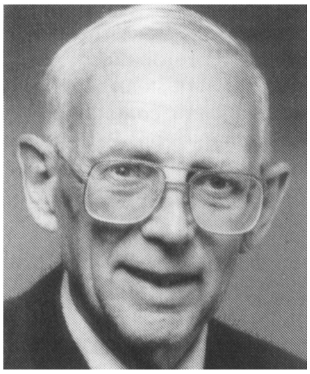
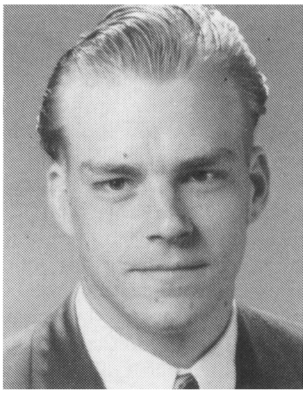


Figure 2 Examples of homolytic and heterolytic processes and catalysis of the latter by Lewis acid A. Dipoles of different bond lengths forming partial charges $\sigma +$ and $\sigma -$ are indicated by bold arrows. R represents any typical carbon structure whose carbenium ion is stable in solution on the timescale of the experiment and X is any ionic leaving group.

During the past half century an enormous amount of effort in physical organic chemistry has gone into the determination of the rates of reactions proceeding through free radical or heterolytic pathways. For example, the enormous literature on solvolytic reactions has provided a firm empirical base for much of modern mechanistic organic chemistry. However, actual experimental values for homolytic and heterolytic bond energies are disproportionately few in number, relative to their fundamental importance, and until recently there have been virtually no cases



Edward M. Arnett was born (1922) and educated in Philadelphia, Pennsylvania. After postdoctoral work at Harvard with Paul D. Bartlett he began his academic career at the University of Pittsburgh (1957—80) from which he moved to Duke (1980—93) where he has been R.J. Reynolds Professor of Chemistry. His interests in physical organic chemistry have emphasized the thermodynamics of formation, solvation, and reaction of organic acids and bases especially carbenium ions and carbanions.



Robert Flowers was born in 1964 in Easton, PA. He received his B.S. from East Stroudsburg University and his Ph.D. (with J. W. Larsen) from Lehigh University in 1991. He is currently a postdoctoral Research Associate at Duke University working with Edward M. Arnett. His principal research interests lie in physical organic chemistry and materials science.

where both modes of bond fission were determined experimentally for the same bonds in the same compounds This should not be surprising in view of the clear dichotomy between the two types of bond fission and the fact that a given type of compound will usually be predisposed to cleave either by homolysis or heterolysis by virtue of its structure and the experimental conditions It is unlikely that it will cleave by both routes simultaneously, although this is not out of the question if the energetics for both pathways are nearly equivalent

This article provides a brief review of new experimental methods which have developed in several laboratories, including ours, which finally make it feasible to determine experimentally the energies for breaking specific bonds in a wide diversity of compounds by both pathways and thereby provide direct comparison of their homolytic and heterolytic bond energies

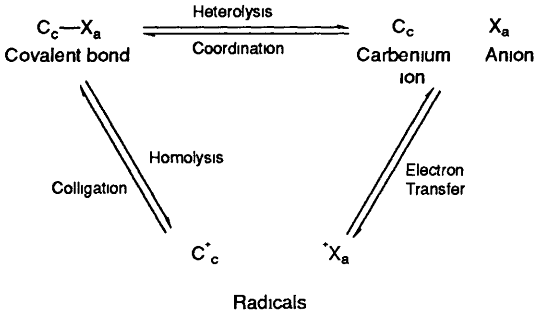


Figure 3 Relationship between various processes for two-electron bond making, breaking, and electron transfer

Figure 3 indicates that the crucial information for relating heterolytic and homolytic bond energies is the energy for transferring one electron from the anion to the cation to produce the pair of free radicals Although this relationship has been understood formally for a long time the experimental means for relating the different steps has only become available recently through the development of several new electrochemical techniques which permit the measurement of electron transfer energies on a time scale so rapid that the very high reactivities of the radical or ionic species which form at the electrodes cannot intrude on the measurements Naturally, the more stable the species the more straightforward and reliable the measurements will be, but modern electrochemical techniques permit the measurement of a surprisingly wide range of electron transfer energies

2 Formation of Radicals, Carbenium Ions, and Carbanions

In order to break a bond in a stable molecule an amount of energy must be invested which is thermodynamically equivalent to its strength This energy can be provided thermolytically, through heating to high temperatures, or photolytically by exciting the molecule to be cleaved with high energy radiation and both of these methods have been applied, especially to homolytic cleavage More familiarly, bonds may be broken by the attack of reactive chemical species (*e g* , radicals, carbenium ions, carbanions) In such processes the energy to break the old bonds is paid for by the formation of the stabler new ones

One of the most thoroughly studied, and by now thoroughly established, principles in physical organic chemistry is that the thermodynamics and kinetics of reaction are usually related This relationship is especially close if the energy change is large [1] Thus it is intuitively attractive to believe that very endothermic processes which require the investment of much energy for bond scission will be slow and that highly exothermic reactions will be very fast This relationship is by now supported by many experimental data and also stands on a firm theoretical basis [2] The authoritative 1982 review by McMillen and Golden[3] and Benson's classic monograph[4] summarize the application of high energy cleavage methods, mostly in the gas phase, to the determination of homolytic bond energies and present the evaluated data in useful tabular form

This approach was also applied for many years to the study of heterolytic reactions through the comparison of solvolysis rates An enormous background of information was obtained on the relative stabilities of carbenium ions on the assumption that they were close in structure and energy to the transition states for the solvolysis reactions The presumed relationship between these rate studies and the actual thermodynamics for heterolytic bond cleavage to form the carbenium ions was finally placed on a firm experimental basis in our laboratory in the 1970s when we developed a calorimeter that was capable of measuring the heats of reaction of various alkyl and aralkyl halides with very strong Lewis acids (*e g* $SbCl_5$) in solvents (*e g* SO_2ClF) which were so weakly nucleophilic and non-basic that the resulting ions were stable at low temperatures on the timescale of the calorimetric experiment [5] [9] These results provided for the first time real thermochemical data for comparing the *relative* strengths of a variety of bonds between simple alkyl structures and electronegative functions bound to them under a common set of conditions in solution Figure 4 shows their correlation with the absolute values obtained in the gas phase Also, importantly, the solution-phase calorimetric results correlated closely with a number of the solvolytic data, Figure 5, which were presumed previously to be direct expressions of carbenium ion stability [7]

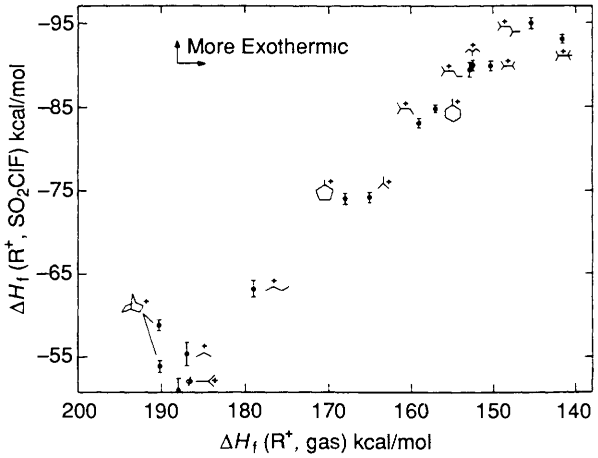


Figure 4 Comparison of heats of formation of simple carbenium ions by solution calorimetery from reaction of alkyl chlorides with SbF_5 in SO_2ClF at − 55 °C and in the gas phase

(Reproduced by permission from E M Arnett and N J Pienta *J Am Chem Soc* 1980 **102** 3329)

While the heterolytic studies of carbenium ion formation were under way a comparable effort in determining the relative energies of carbanion formation were occurring, principally in the laboratory of Professor F G Bordwell who was using the 'super-base' system of dimethlysulfoxide (DMSO) containing its strongly basic potassium salt (K^+ DMSYL) to remove the most acidic protons from a wide variety of compound types to produce their anions in this solvent system [10] The pK_a data obtained by Bordwell gave free energies of ionization which corresponded closely to the heats of deprotonation (ΔH_{dep}) obtained in our laboratory by the injection of small samples of the protonic acids into a calorimeter containing the K^+ $DMSYL^-$/DMSO superbase system Not only was there a good correlation between free energies and enthalpies of deprotonation in DMSO, but these values correlated well with the corresponding gas phase acidities

3 Heats of Heterolysis of Carbon–Carbon Bonds

As a result of the calorimetric experiments described above the conditions for measuring the heats of formation of many types

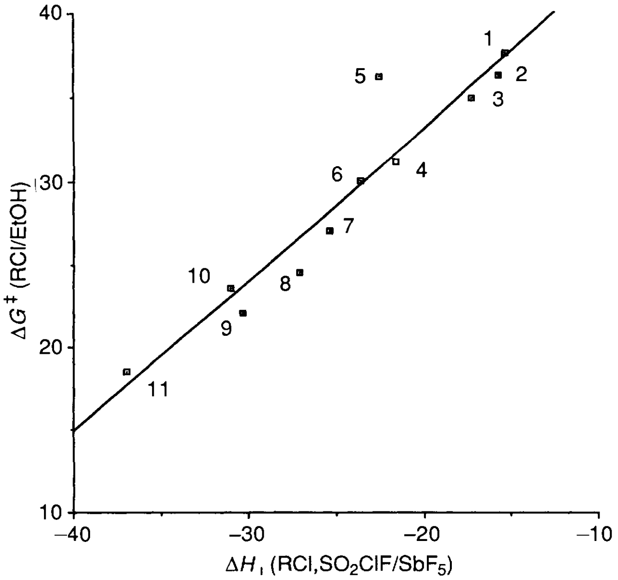


Figure 5 Correlation of free energies of activation for ethanolysis of alkyl chlorides *vs* heats of ionization in SO_2ClF (1) 2-propyl chloride (2) 2-butyl chloride, (3) cyclopentyl chloride (4) 1 adamantyl chloride (5) cyclohexyl chloride, (6) 2-*exo*-norbornyl chloride (7) t-butyl chloride, (8) 1-methylcyclopentyl chloride, (9) 2-phenyl-2-propyl chloride (10) 2-methyl-2-*exo*-norbornyl chloride (11) 2-phenyl-2-*exo*-norbornyl chloride

of carbenium ions in superacidic media, and of carbanions, and other types of organic anions, in superbases were well established and the limits of their stabilities with regard to attacking the solvent as an acid or a base were firmly delineated These experiments laid the background for an alternative approach to the thermolytic and photolytic ones mentioned above for the determination of bond energies The first law of thermodynamics indicates that a bond energy may be determined precisely either by measuring the energy required to break it, as in the thermolytic and photolytic experiments, or by the heat of reaction which is liberated if the component radicals, carbenium ions, and anions react together in a calorimeter Thus the heat of heterolysis (Figure 3) is exactly equal to the heat of coordination measured from the reaction of suitable salts of the carbenium ion and carbanion in an appropriate solvent

The feasibility of studying such cation/anion reactions was established clearly in our laboratory in 1983 when we learned that the rates and equilibria for the reactions of a variety of carbenium ions and anions covered the entire range from instantaneous, complete, and exothermic processes to those which were so favourably on the side of the ions that after six months there was still no evidence for reaction occurring [11]

Against this background it is clear how reaction calorimetry may be employed for the determination of heterolysis energies Salts of carbenium ions and anions which are sufficiently stable to be prepared as separate solutions in an appropriately robust solvent are mixed suddenly in a calorimeter The heat of reaction (coordination) is measured and the sign changed to give ΔH_{het} The covalent product which is formed must be produced rapidly, completely, and cleanly with the new bond in a clearly identifiable structural position

The requirement of an appropriate solvent is severe if a wide range of carbenium/carbanion reactions is to be studied because the solvent must neither react as a nucleophile or base with the carbenium ion nor as an acid to transfer a proton to strongly basic anions In practice, the limitations on the process are the use of cations and anions which are sufficiently stabilized by resonance so that they will not attack the solvent of choice, tetramethylene sulfone (sulfolane), a remarkably robust liquid that can stand up to the attack of many species of both types but which is still vulnerable to attack by the most reactive members of both types of ions

4 Heats of Homolysis (ΔH_{homo}) from ΔH_{het}s and Redox Potentials

With such a straightforward means for determining heterolysis energies in hand, the question of their conversion into heats of homolysis (ΔH_{homo}) has also become approachable through the applications of new electrochemical techniques Referring again to Figure 3, the electron transfer energy, which represents the energy for transfer of an electron from the carbanion to the carbenium ion to produce the corresponding radicals, allows completion of the cycle and calculation of the energy of homolysis for the same bond for which ΔH_{het} was determined calorimetrically

The electron transfer energies are obtained as the sums of the oxidation potentials of the anions and the reduction potentials of the carbenium ions Although electrochemical cells have been constructed which allow the direct determination of the half-cell potentials for highly stable ions of both types, the free radicals which are produced by oxidizing many organic anions and reducing many carbenium anions are so reactive and undergo such rapid decomposition at the electrode that special methods must be employed to determine their redox potentials Cyclic voltammetry (CV) is the favoured technique which has been developed for this purpose The potential on a microelectrode placed in the solution is cycled so rapidly that the radicals which are produced by oxidation of the anion or reduction of the cation are immediately reduced or oxidized back to their original states before they can undergo reaction in the neighbourhood of the electrode By going through the oxidation–reduction cycle 50 or 100 times a second most decomposition reactions can be 'outrun' by the electrochemical cycle In some cases (*e g*, phenoxide anions) where reversible voltammagrams are hard to obtain because of radical instability, complementary electrochemical techniques have been used – second harmonic alternating current voltametry (SHACV) and Osteryoung squarewave voltammetry (OSWV)

These methods have been employed in several laboratories, including our own, to obtain oxidation potentials for highly sensitive substituted phenoxide anions When these E_{ox} values are combined with acidity values (pK_as) for the parent phenols, bond dissociation energies (BDEs) are obtained that lie within experimental error of the values determined by the more traditional photolysis or thermolysis methods [12] [16] It is very important to appreciate the agreement of these totally independent methods Without them there remains a lingering reasonable doubt that the various numbers for the electron transfer energies and the derived ΔH_{homo}s might be seriously in error and simply be the products of combining virtually meaningless experimental values It is surprising that in a number of cases even irreversible redox potentials obtained through cyclic voltammetry have agreed within experimental error with values obtained by the more sophisticated SHACV and OSWV techniques

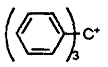
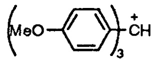
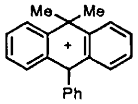
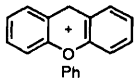
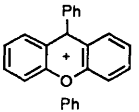
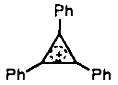
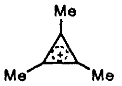
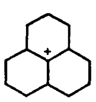
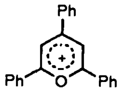
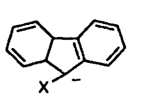
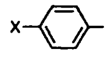
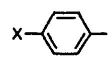
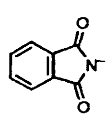
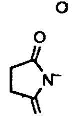
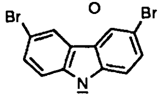
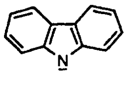
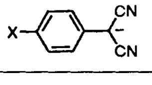
In addition to the problem of the reversibility of the electrode process is the fundamental difficulty of combining calorimetric heats of reaction ΔH_{het} with electrochemical electron transfer energies which are actually free energy terms

$$\Delta G_{ET} = -23\ 06[E_{red}(C_i^+) - E_{ox}(X_i^-)] \qquad (1)$$

Free energy and enthalpy terms can only be combined if entropy terms are negligible It turns out that this is usually true for the processes we have studied In a number of cases the entropies of electron transfer were determined by measuring the redox potentials at a series of temperatures and have been used to correct the observed electron transfer energies to enthalpies of electron transfer In all cases studied so far the entropy terms are so insignificant that it appears to be a generally safe approximation, to the nearest 1—2 kcal/mol, simply to combine the ΔG_{ET} with ΔH_{het}

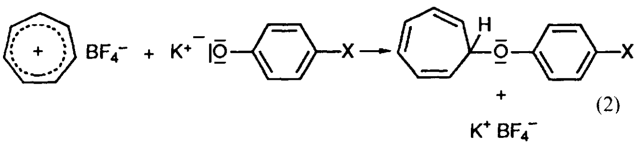
Table 1 presents the structures of the various groups of carbenium ions and anions for which we have determined

Table 1 Structures of the cations and anions The counterion for the cations is tetrafluoroborate and for the anions is potassium Abbreviations Me, methyl, Ph, phenyl, G = phenyl, phenylthio, cyano, methoxycarbonyl, or phenylsulfonyl X = nitro, cyano, carbomethoxy, bromo, chloro, fluoro, t-butyl, methyl, methoxy, or hydrogen

Ion	Structure
Trityl	
4,4′-Dimethoxydiphenylmethyl	
9,9′-Dimethyl-10-phenyl-9,10-dihydroanthracenium	
Xanthylium	
9-Phenylxanthylium	
Triphenylcyclopropenylium	
Tropylium	
Trimethylcyclopropenylium	
Perinaphthenium	
2,4,6-Triphenylpyrylium	
9-G-Fluorenide	
4-X-Phenoxide	
4-X-Thiophenoxide	
Phthalimide anion	
Succinimide anion	
3,6-Dibromocarbazole anion	
Carbazole anion	
4-X-Phenylmalononitrile	

ΔH_{het}s, ΔG_{ET}s, and ΔH_{homo}s Nearly 300 combinations of cations and anions have been studied in sulfolane at 25 °C, containing 5% 3-methylsulfolane to reduce the melting point since pure sulfolane melts at 26 °C In all cases the reactions were complete and instantaneous on the time scale of the thermometric titration and, in a number of cases, the product was isolated and its structure verified by nuclear magnetic resonance when there could be some ambiguity regarding the position of reaction between the carbenium ion and the anion

A typical presentation of data is Table 2 for the seven compounds formed by reaction of the relatively stable carbenium ion salt, tropylium tetrafluoroborate with the potassium salts of the *para*-substituted phenols listed in 95% sulfolane/5% 3-methlysulfolane at 25 °C

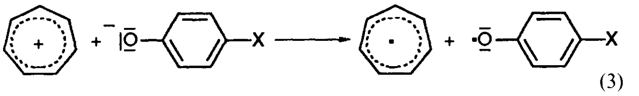


(2)

Thanks to the seven-fold symmetry of the tropylium ion there is no ambiguity about the point of attachment of the phenoxide ions, as there might be, say, for attack by triarylmethylium cations where bond formation might occur on the central methylium carbon or on one of the *para* positions of a phenyl ring Naturally, the heats of reaction, ΔH_{rxn}, that are measured in the calorimeter are exothermic and carry a negative sign, but, since $\Delta H_{\mathrm{het}} = -\Delta H_{\mathrm{rxn}}$, the heats of heterolysis of the stable covalent products are positive, showing that anywhere from 10 64 to 20 25 kcal/mol are needed to cleave the bonds of the compounds in Table 2 back to their original ions

In order to derive the corresponding heats of homolysis, ΔH_{homo}, the oxidation potentials of the phenoxide ions and the reduction potential of the tropylium ion are needed The latter is comparatively easy to obtain by ordinary cyclic voltammetry However, phenoxide ions are notoriously sensitive to oxidation and ordinary CV was incapable of giving reversible behaviour Accordingly, we employed the SHACV technique to obtain the values listed Despite serious questions about the reliability of this method[17] and the unsymmetrical cyclic voltammograms obtained, we have found surprisingly good agreement between our SHACV values for E_{ox} and those obtained by others[18] using CV

Combining E_{ox} for phenoxide ions and E_{red} for tropylium gives the electron transfer energy for the following process in millivolts which are then converted to kcal/mol by multiplication with 23 06 kcal/electron volt If we assume that the entropies for electron transfer are negligible the ΔH_{homo}s are obtained immediately by adding the ΔH_{het}s and the ΔG_{ET}s according to Figure 3



(3)

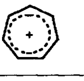
What then is the relation between ΔH_{het} and ΔH_{homo} for the series of compounds whose C—O bonds were formed by reaction in the calorimeter? Figure 6 which compares ΔH_{het} with ΔH_{homo} for all 60 carbenium-phenoxide products shows a totally chaotic scatter of points Although some families of compounds give fair correlation lines, most of them do not and there is no doubt that a general correlation is out of the question

The ionization of a phenol in basic solution by removing a proton and leaving a phenoxide ion may also be considered as a heterolytic process Figure 7 shows the close correlation between ΔG_i (i e 1 36 p*K*a) for breaking the O—H bonds of the phenols by transfer of a proton to K^+ DMSYL$^-$ in DMSO and ΔH_{het} for breaking the corresponding O—C bonds between the phenoxy and tropylium residues in Table 1

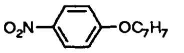
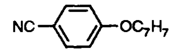
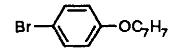
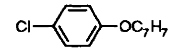
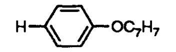
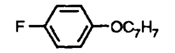
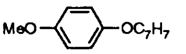
This raises the interesting question as to whether it is possible to model heterolysis behaviour in general terms by the stabilities

Table 2 Heats of heterolysis, free energies of single electron transfer, and heats of homolysis from tropylium phenoxides and pK_as, $E_{1/2}$, and BDEs for substituted phenoxides

Tropylium ion



$E_{\mathrm{red}}\mathrm{C}^+$ = − 0 622 ± 0 002 V
pK_{R} = 4 70

Compound	ΔH_{het}[C–X] (kcal/mole)	$E_{1/2}$(X$^-$) (V)	ΔG_{ET} (kcal/mole)	ΔH_{homo} (kcal/mole)	pK_a	BDE (kcal/mole)
	10 64 ± 0 66	0 255 ± 0 015	20 22 ± 0 35	30 86 ± 0 75	10 78	93 80 ± 0 39
	13 25 ± 0 34	0 080 ± 0 010	16 19 ± 0 23	29 44 ± 0 41	13 20	93 08 ± 0 27
	20 48 ± 0 52	− 0 287 ± 0 015	7 73 ± 0 35	28 21 ± 0 63	16 36	88 95 ± 0 39
	16 98 ± 0 49	− 0 116 ± 0 017	11 67 ± 0 39	28 65 ± 0 63	16 75	93 42 ± 0 43
	17 34 ± 0 42	− 0 270 ± 0 010	8 12 ± 0 24	25 46 ± 0 48	18 03	91 63 ± 0 27
	18 19 ± 0 29	− 0 294 ± 0 010	7 56 ± 0 23	25 75 ± 0 37	18 10	91 17 ± 0 27
	20 04 ± 0 40	− 0 563 ± 0 014	1 36 ± 0 33	21 40 ± 0 52	19 10	86 33 ± 0 36

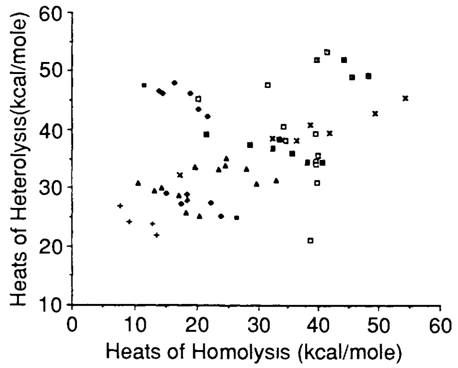


Figure 6 ΔH_{het} *vs* ΔH_{homo} for compounds formed from reactions of eight phenoxide anions with nine carbenium ions
(Reproduced by permission from E M Arnett, K Amarnath, N G Harvey, and S Venimadhavan, *J Am Chem Soc* , 1990, **112**, 7346)

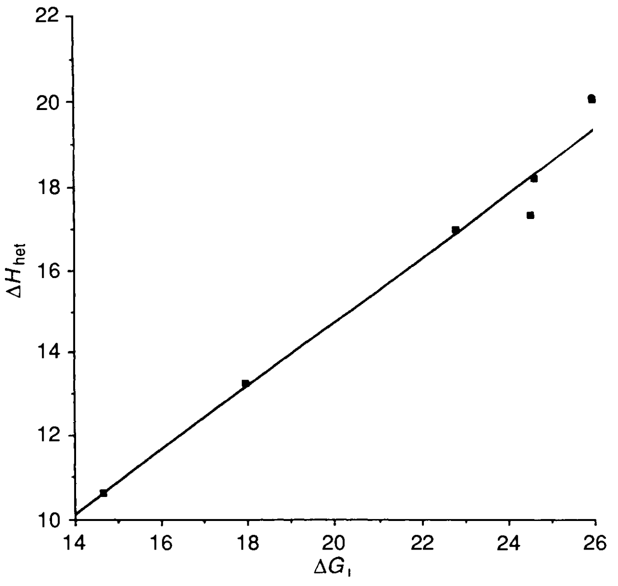
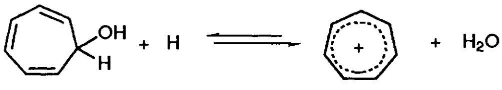


Figure 7 Comparison of ΔH_{het} for breaking O–C bonds to produce the tropylium cation and substituted phenoxy anions with free energies for ionization of the corresponding O–H bonds

of the anions and cations that are produced by this mode of bond cleavage



(4)

Just as anion stabilities are compared by their proton transfer energies to basic solution in terms of pK_as, carbenium ion stabilities are compared by the ionization energies of their carbinols in aqueous acid solution for the following process (*e g* , as applied to the tropylium ion) The relative stabilities of many carbenium ions have been arranged on the so-called pK_{R^+} scale by the ionization equilibrium constants for their corresponding carbinols in a series of aqueous sulfuric acid solutions [19] Since Figure 7 shows the correlation between the energies for breaking the bonds from phenoxide to the proton and to the tropylium ion it seems reasonable that there should be a general equation relating the heterolysis energies to the sum of the stabilities of the phenoxide ions, pK_a, and those of the carbenium ions, pK_{R^+}

$$\Delta H_{\mathrm{het}} = a\mathrm{p}K_a + b\mathrm{p}K_{\mathrm{R}} + c \qquad (5)$$

where *a*, *b*, and *c* are constants Figure 8 confirms this surprisingly simple relationship which we have shown to apply, with only minor modifications, for hundreds of C–C, C–O, C–N, and C–S bonds [20-23]

Just as pK_as may be considered as free energies of heterolysis for breaking the phenolic O–H bonds, the corresponding bond dissociation energies (BDE) represent their homolytic bond energies A cycle equivalent to Figure 3 allows conversion of phenolic pK_as to their BDEs using E_{ox} for the phenoxide ion and the E_{red} for the proton Such calculations have been made by Bordwell,[24] Brauman,[25,26] Arnold,[27] and Friedrich[28] and we have included BDEs derived in this way using our E_{ox}s and Bordwell's pK_as, assuming that they would vary little from DMSO to sulfolane, two polar solvents of rather similar structures

These homolytic bond energies are of particular value for validating the whole series of assumptions on which our calculations of ΔH_{homo}s are based Table 3 compares BDEs for some phenols calculated from our data with those which Merenyi *et al* [12] have determined recently by pulse radiolysis, a totally different route The generally good agreement lends support to both methods

5 Cleavage of Radical Ions

As can be seen above, the combination of calorimetric and electrochemical measurements provides a powerful entree to the

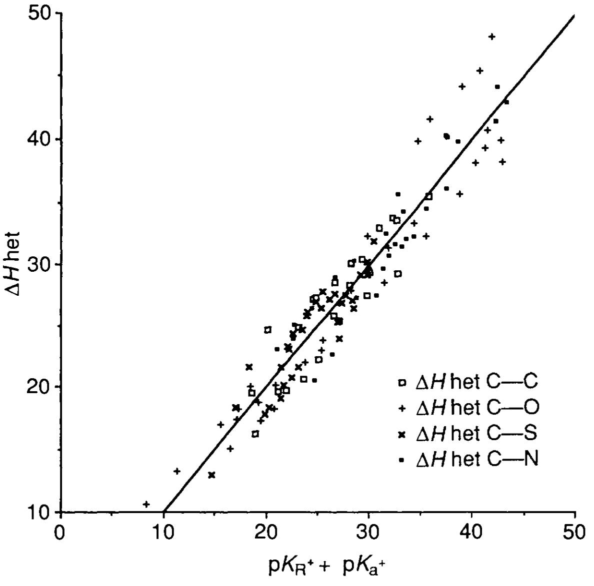


Figure 8 Relationship between ΔH_{het} and ion stability properties (pK_as and pK_R s) for one hundred and fifty C–C C–O, C–S, and C–N bonds

Table 3 Comparison of bond dissociation energies (BDE's) of phenols by two different methods

Phenol	BDE[a]	BDE[b]
4-H	91.63 ± 0.27	88.2 ± 0.5
4-Me	87.15 ± 0.41	86.1 ± 0.5
4-F	91.17 ± 0.27	87.4 ± 0.5
4-Cl	93.42 ± 0.43	87.6 ± 0.5
4-NO_2	93.80 ± 0.39	94.2 ± 1.4
4-OMe	86.33 ± 0.36	82.6 ± 0.5
4-t-Bu	89.89 ± 0.36	
4-CN	93.08 ± 0.27	92.9 ± 0.7
4-Br		88.1 ± 0.5
4-OCOMe	88.88 ± 0.36	90.3 ± 0.5
4-I		87.9 ± 0.5

[a] Values determined using Bordwell's equation BDE = 1.37pK_a + 23.06E_{ox}(A) + 55.86 (see ref 21). [b] Values from ref 12.

determination of heterolysis and homolysis energies provided that the carbenium ions and the corresponding anions are sufficiently stable that they do not attack the solvent sulfolane, or suffer any other fate, before being brought into reaction together. However, it is possible even to go beyond that to the determination of bond cleavage energies for the highly reactive radical cations and radical anions that are produced by the oxidation and reduction of the same neutral species for which we have determined ΔH_{het} and ΔH_{homo}.

Radical ions are familiar species in gas phase mass spectrometry and also have been the subject of extensive research in solution.[29] However, most investigations have been limited to the examination of examples of either type of species with relatively few reports describing kinetic or thermodynamic information for both kinds of radical ions derived from the same neutral precursor. No previous study to our knowledge has related such measurements to the corresponding homolysis and heterolysis energies of the same neutral precursors as those for the radical ions. Thanks again to the rapid scanning electrochemical techniques it is possible to obtain redox potentials for many of the neutral molecules described above and to obtain thereby the free energies of formation of the radical cations and radical anions. As Equations 6 and 7 show, it is possible to combine these data with ΔH_{het}s for the neutral species and the redox potentials of the associated carbenium ions and anions to obtain the heats of cleavage of the radical cations and radical anions.

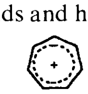
$$\Delta H_{cleav}[C-X]^{\dot{+}} = \Delta H_{het}[C-X] + 23.06\{E_{ox}(X\ ) - E_{ox}[C-X]\} \tag{6}$$

$$\Delta H_{cleav}[C-X]^{\dot{}} = \Delta H_{het}[C-X] + 23.06\{E_{red}[C-X] - E_{red}(C^+)\} \tag{7}$$

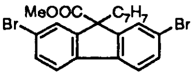
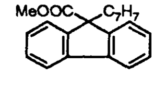
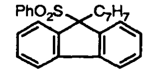
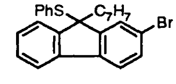
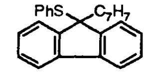
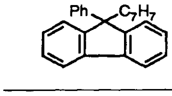
Table 4 presents the complete set of data for the six compounds produced from the reaction of tropylium ion with six substituted fluorenyl anions. Note that the ΔH_{cleav} values for the radical cations are actually strongly exothermic indicating that, from a thermodynamic standpoint, there is nothing holding the resulting radical and cation together once the electron has been taken away from the neutral species. Although the activation barriers for these cleavages have not been measured there is

Table 4 Heats of heterolysis and homolysis of neutral compounds and heats of cleavage of radical cations and radical anions

Tropylium ion



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

Compound	$\Delta H_{het}[C-X]^a$ (kcal/mol)	ΔG_{ET} (kcal/mol)	ΔH_{homo} (kcal/mol)	[AOP + CRP]	$E_{ox}[C-X]^{\dot{+}}$ (V)	$E_{red}[C-X]^{\dot{}}$ (V)	$\Delta H_{cleav}[C-X]^{\dot{+}}$ (kcal/mol)	$\Delta H_{cleav}[C-X]^{\dot{}}$ (kcal/mol)
	19.45 ± 0.11	7.75	27.20	10.2	+ 1.519 ± 0.018	− 1.000 ± 0.023	− 22.17	10.69
	24.89 ± 0.53	1.55	26.44	10.7	+ 1.475 ± 0.020	− 1.173 ± 0.015	− 21.92	12.14
	27.17 ± 0.54	5.30	32.47	14.7	+ 1.632 ± 0.020	− 1.540 ± 0.021	− 19.50	5.95
	28.59 ± 0.12	−2.54	26.05	9.10	+ 1.590 ± 0.023	− 1.335 ± 0.020	− 22.42	12.10
	30.52 ± 0.45	−6.00	24.52	8.66	+ 1.439 ± 0.019	− 1.370 ± 0.015	− 23.00	13.23
	33.84 ± 0.32	−11.1	22.79	7.03	+ 1.394 ± 0.025	− 1.430 ± 0.020	− 23.69	15.16

every reason to believe, based on Hammond–Marcus principles, that the two product particles should separate almost as rapidly as they are formed

Looking at the ΔH_{cleav} values for the radical anions, there is definitely some thermodynamic stability for these species but it is relatively small and again one may expect that cleavage will occur rapidly once an electron is added to the neutral compounds on the left

Cleavage of both types of species raises the question as to how the bond is broken – which portion ends up as a radical and which portion as an ion In the cases of the six compounds in Table 4 it is quite clear that the radical cations go to produce tropylium cations, which are readily demonstrable in the cyclic voltammograms and, correspondingly, the radical anions are decomposed to produce fluorenyl anions and tropylium radicals The data for the radical ions shown in Table 4 are reasonably well substantiated However, in other studies of the compounds produced through the ΔH_{het} determinations, the radical anions were so unstable that even by the fastest electrochemical techniques at our disposal we were unable to obtain reliable reduction potentials for their formation from the neutrals

Acknowledgements We are glad to recognize the contributions of Drs Venimadhavan, N Harvey, J -P Cheng, K Amarnath, E G Troughton, K E Molter, and B Chawla to the work described here and for the financial support by the National Science Foundation and the Gas Research Institute which made it possible

6 References

1 G S Hammond, *J Am Chem Soc*, 1955, **77**, 334
2 R A Marcus, *Annu Rev Phys Chem*, 1964, **15**, 155
3 D F McMillen and D M Golden, *Annu Rev Phys Chem*, 1982, **33**, 493
4 S W Benson, in 'Thermochemical Kinetics', 2nd edn, Wiley-Interscience, New York, 1976, p 1
5 E M Arnett and J W Larsen, *J Am Chem Soc*, 1968, **90**, 791
6 E M Arnett and S C Petro, *J Am Chem Soc*, 1978, **100**, 1978
7 E M Arnett, S C Petro, and P von R Schleyer, *J Am Chem Soc*, 1979, **101**, 522
8 E M Arnett and N J Pienta, *J Am Chem Soc*, 1980, **102**, 3329
9 E M Arnett and T C Hofelich, *J Am Chem Soc*, 1983, **105**, 2889
10 F G Bordwell, *Acc Chem Res*, 1988, **21**, 456
11 E M Arnett, E B Troughton, and K E Molter, *J Am Chem Soc*, 1984, **106**, 6726
12 J Lind, X Shen, T E Eriksen, and G Merenyi *J Am Chem Soc*, 1990, **112**, 479
13 S G Lias, J E Bartmess, J F Biebman, J L Holmes, R D Levin, and W G Mallard, *J Phys Chem Ref Data*, 1988, 17, Suppl No 1
14 T B Macmahon and P J Kebarle, *J Am Chem Soc*, 1977, **99**, 2222
15 M Fujio, R T McIver, Jr, and R W Taft, *J Am Chem Soc*, 1981, **103**, 4017
16 P Mulder, O W Saastad, and D Griller, *J Am Chem Soc*, 1988, **110**, 4090, and references therein
17 E Ahlberg and V Parker, *Acta Chem Scand Ser B*, 1980, **34**(**2**), 91
18 F G Bordwell and J P Cheng, *J Am Chem Soc*, 1991, **113**, 1736
19 D Bethell and V Gold, in 'Carbonium Ions an Introduction', Academic Press, New York, 1967, p 76
20 E M Arnett, B Chawla, K Amarnath, and L G Whitesell, Jr, *Energy & Fuels*, 1987, **1**, 17
21 E M Arnett, K Amarnath, N G Harvey, and S Venimadhavan, *J Am Chem Soc*, 1990, **112**, 7346
22 E M Arnett, S Venimadhavan, and K Amarnath, *J Am Chem Soc*, 1992, **114**, 5598
23 S Venimadhavan, K Amarnath, N G Harvey, J -P Cheng, and E M Arnett, *J Am Chem Soc*, 1992, **114**, 221
24 F G Bordwell and M J Bausch, *J Am Chem Soc*, 1986, **108**, 1979
25 B K Janousek and J I Brauman, in 'Gas Phase Ion Chemistry' ed M T Bowers, Academic Press, New York, 1979, 53
26 J I Brauman, in 'Frontiers of Free Radical Chemistry', ed W A Pryor, Academic Press, New York, 1980, 23
27 A Nicholas, P Mide, and D R Arnold, *Can J Chem*, 1982, **20**, 2165
28 L E Friedrich, *J Org Chem*, 1983, **48**, 3851
29 M Chanon, M Rajzmann, and F Chanon, *Tetrahedron*, 1990, **46(18)**, 6193