

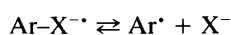
Heterolytic Bond Dissociation Energies of Halobenzene Anion Radicals

Vernon D. Parker

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, USA

Parker, V. D., 1992. Heterolytic Bond Dissociation Energies of Halobenzene Anion Radicals. – Acta Chem. Scand. 46: 307–308.

The formation of anion radicals of halobenzenes is accompanied by a severe weakening of the carbon–halogen bonds and subsequent unimolecular cleavage of halide ion. This reaction is the key step in the $S_{RN}1$ mechanism.¹ Although a wealth of kinetic data exists for reaction (1), no quantitative data are available concerning the driving force. We now report the first heterolytic bond dissociation energies for the halobenzene anion radicals.



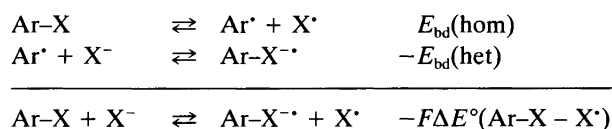
Electrode potential measurements, by way of thermochemical relationships,² provide access to a wealth of thermochemical data which are either difficult or impossible to obtain directly.^{3–9} The isodesmic reaction relationship¹⁰ which provides anion radical heterolytic bond dissociation energies [$E_{\text{bd}}(\text{het})$] is illustrated in Scheme 1. The difference between the homolytic bond dissociation energy [$E_{\text{bd}}(\text{hom})$] of the aryl halide substrate and $E_{\text{bd}}(\text{het})$ above

the line is directly proportional to the difference in reduction potentials of Ar-X and X^{\cdot} below the line. For the halobenzenes, the pertinent electrode potential data¹¹ and the difference, $\Delta E_{\text{bd}}(\text{hom-het})$, are summarized in Table 1.^{12,13}

The known $E_{\text{bd}}(\text{hom})$ of halobenzenes¹⁴ listed in Table 2 are gas phase enthalpy values and do not apply directly to Scheme 1. It is commonly observed that homolytic E_{bd} do not change significantly on going from the gas phase to solution.⁵ This implies that free energy [$E_{\text{bd}}(\text{hom})_G$] in acetonitrile solution can be derived from the corresponding enthalpy [$E_{\text{bd}}(\text{hom})_H$] value by application of eqn. (2)

$$E_{\text{bd}}(\text{hom})_G = E_{\text{bd}}(\text{hom})_H - T [S_f^\circ(\text{X}^{\cdot}) + \Delta S_{\text{sol}}^\circ(\text{X}^{\cdot})] \quad (2)$$

which requires the usual assumption¹⁵ that the entropy terms for Ar-X and Ar^{\cdot} cancel. A difficulty associated with

Heterolytic bond dissociation energies of $\text{Ar-X}^{\cdot-}$ 

Scheme 1.

Table 1. Bond dissociation energy differences from electrode potential data.^a

Quantity	Ph-F	Ph-Cl	Ph-Br
$E^\circ(\text{Ph-X})/\text{V vs. NHE}$	-2.73	-2.54	-2.20
$E^\circ(\text{X}^{\cdot})/\text{V vs. NHE}$	2.9	2.1	1.7
$\Delta E_{\text{bd}}(\text{hom-het})_G/\text{kcal mol}^{-1}$	130	107	90

^aElectrode potentials are from Ref. 11; $\Delta E_{\text{bd}}(\text{hom-het})_G$ were calculated from the relationship in Scheme 1.

Table 2. Heterolytic bond dissociation energies of halobenzene anion radicals.

Anion Radical	$E_{\text{bd}}(\text{Ph-X})^a$	$S_f^\circ(\text{X}^{\cdot})^b$	$E_{\text{bd}}(\text{het})/\text{kcal mol}^{-1}$		
			Maximum	Minimum	Estimate
Ph-F ^{·-}	126	37.9	-4	-15	-10
Ph-Cl ^{·-}	96	39.5	-11	-23	-18
Ph-Br ^{·-}	81	41.8	-9	-22	-17

^a $E_{\text{bd}}(\text{kcal mol}^{-1})$ are gas phase enthalpy values from Ref. 14. ^bEntropies of formation ($\text{cal K}^{-1} \text{mol}^{-1}$) are from Ref. 16.

applying eqn. (2) is that while the pertinent entropies of formation [$S_f^\circ(X^*)$] are available,¹⁶ the corresponding solvation terms [$\Delta S_{\text{solv}}^\circ(X^*)$] are not. In related work dealing with C-H⁵ and Metal-H^{7a} E_{bd} which require $\Delta S_{\text{solv}}^\circ(\text{H}^*)$ this term was approximated using the known entropy of solvation of the hydrogen molecule. This results in an uncertainty in the derived E of unknown magnitude.

The $E_{\text{bd}}(\text{het})_G$ values for the dissociation of Ph-X^{-•} in acetonitrile solution listed in Table 2 are maximum and minimum estimates based on extreme values of $\Delta S_{\text{solv}}^\circ(X^*)$. The maximum values assume $\Delta S_{\text{solv}}^\circ(X^*)$ to be equal in magnitude but opposite in sign to $S_f^\circ(X^*)$ while the minimum values assume the solvation term to be insignificant. For reasons discussed in the following paragraph the true value is believed to lie approximately midway between the extremes.

The entropy changes accompanying the dissolution of gaseous atoms or molecules are negative. There are limited data available in non-aqueous solvents. For example, $\Delta S_{\text{solv}}^\circ(\text{H}_2)$ is equal to -11.9 and -12.0 cal K⁻¹ mol⁻¹ in acetonitrile and dimethyl sulfoxide, respectively.¹⁷ The entropies of solvation of He, N₂, Ar, and C₂H₆ in *N*-methylacetamide have been reported to be -12.0 , -14.9 , -15.0 , and -17.8 cal K⁻¹ mol⁻¹.¹⁸ The data suggest at least a weak dependence on atomic or molecular volume. On this basis, Ar would appear to be a reasonable model for Cl[•] and together with the apparent insensitivity to solvent this leads to an estimate of -15 cal K⁻¹ mol⁻¹ for $\Delta S_{\text{solv}}^\circ(\text{Cl}^*)$. This last column in Table 2 gives an estimate of the true value arrived at by assuming -15 cal K⁻¹ mol⁻¹ for the entropy of solvation of all the halogen atoms in acetonitrile.

It should be pointed out that the approximation, $\Delta S_{\text{solv}}^\circ(\text{H}^*)$ is equal to $\Delta S_{\text{solv}}^\circ(\text{H}_2)$ in acetonitrile, leads to calculated¹⁰ E_{bd} which are within 1 kcal mol⁻¹ of those determined by calorimetric methods for Metal-H compounds.¹⁹ It would appear that Ar is as good a model, in terms of solvation entropy, for Cl[•] as H₂ is for H[•]. Therefore, the $E_{\text{bd}}(\text{het})_G$ in the last column of Table 2 are expected to be reliable. In any event, it can be concluded that the true values lie within the maximum and minimum limits given and most probably close to the estimated values.

Further work is in progress to establish $E_{\text{bd}}(\text{het})_G$ of other anion radicals in solution. Since homolytic E_{bd} of neutral molecules are relatively insensitive, i.e. within a few kcal mol⁻¹, to changes in structure for a given bond type,⁵ differences in $E_{\text{bd}}(\text{het})_G$ can be expected to be approximately proportional to the differences in reduction potentials of Ar-X.¹³ Having access to the thermodynamic driving forces of aryl halide anion radical cleavage reactions will be very useful in mechanistic studies of these important reactions.²⁰

Acknowledgements. This research was supported by the National Science Foundation (CHE-9106618). This support is gratefully acknowledged.

References

- Bunnett, J. F. *Acc. Chem. Res.* 11 (1978) 413.
- The thermochemical relationships apply to isodesmic reactions which allow the free energy change for the transfer of groups or atoms to be equated to that corresponding to the transfer of an electron.¹⁰
- (a) Breslow, R. and Balasubramanian, K. *J. Am. Chem. Soc.* 91 (1969) 5182; (b) Breslow, R. and Chu, W. *ibid.* 92 (1970) 2165; (c) Breslow, R. and Chu, W. *ibid.* 95 (1973) 410; (d) Breslow, R. and Mazur, S. *ibid.* 95 (1973) 584; (e) Wasielewski, M. R. and Breslow, R. *ibid.* 98 (1976) 4222; (f) Breslow, R. and Goodin, R. *ibid.* 98 (1976) 6076; (g) Breslow, R. and Grant, J. *ibid.* 99 (1977) 7745; (h) Breslow, R. and Mazur, S. *ibid.* 95 (1973) 584; (i) Jaun, B., Schwartz, J. and Breslow, R. *ibid.* 102 (1980) 5741.
- (a) Nicolas, A. M. de P. and Arnold, D. R. *Can. J. Chem.* 60 (1982) 2165; Okamoto, A., Snow, M. S. and Arnold, D. R. *Tetrahedron* 22 (1986) 6175.
- (a) Bordwell, F. G. and Bausch, M. J. *J. Am. Chem. Soc.* 108 (1986) 2473; (b) Bordwell, F. G., Cheng, J.-P. and Harrelson, J. A. *ibid.* 110 (1988) 1229; (c) Bordwell, F. G., Cheng, J.-P. and Bausch, M. J. *ibid.* 110 (1988) 2867; (d) *ibid.* 110 (1988) 2872; (e) Bordwell, F. G., Cheng, J.-P., Bausch, M. J. and Bares, J. E. *J. Phys. Org. Chem.* 1 (1988) 209; (f) Bordwell, F. G., Bausch, M. J., Branca, J. C. and Harrelson, J. A. *ibid.* 1 (1988) 225; (g) Bordwell, F. G. and Cheng, J.-P. *J. Am. Chem. Soc.* 111 (1989) 1792; (h) Bordwell, F. G., Harrelson, J. A. and Satish, A. V. *J. Org. Chem.* 54 (1989) 3101.
- (a) Parker, V. D., Tilset, M. and Hammerich, O. *J. Am. Chem. Soc.* 109 (1987) 7905; (b) Parker, V. D. and Tilset, M. *ibid.* 110 (1988) 1649.
- (a) Tilset, M. and Parker, V. D. *J. Am. Chem. Soc.* 111 (1989) 6711; (b) Ryan, O., Tilset, M. and Parker, V. D. *ibid.* 112 (1990) 2618.
- (a) Wayner, D. D. M., McPhee, D. J. and Griller, D. *J. Am. Chem. Soc.* 110 (1988) 132; (b) Griller, D., Simoes, J. A. M., Mulder, P., Sim, B. A. and Wayner, D. D. M. *ibid.* 111 (1989) 7872; (c) Griller, D. and Wayner, D. D. M. *Pure Appl. Chem.* 61 (1989) 717.
- Arnett, E. M., Harvey, N. G., Amarnath, K. and Cheng, J.-P. *J. Am. Chem. Soc.* 111 (1989) 4143; (b) Arnett, E. M., Amarnath, K., Harvey, N. G. and Venimadhavan, S. *ibid.* 112 (1990) 7346.
- Parker, V. D., Handoo, K. L., Roness, F. and Tilset, M. *J. Am. Chem. Soc.* 113 (1991) 7493.
- Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, New York 1987, Chap. 3.
- It has previously been concluded¹³ that the driving force for the anion radical cleavage reaction is composed of the free energy of the bond dissociation of the parent aryl halide and the standard potentials of the ArX/ArX^{-•} and X[•]/X⁻ redox couples.
- Saveant, J.-M. *Adv. Phys. Org. Chem.* 26 (1990) 1.
- McMillen, D. F. and Golden, D. M. *Annu. Rev. Phys. Chem.* 33 (1982) 493.
- For justification of this assumption see Ref. 8(b).
- CRC Handbook of Chemistry and Physics*, Weast, R. C., Ed., CRC Press, Boca Raton, FL 1990.
- Brunner, E. *J. Chem. Eng. Data* 112 (1985) 269.
- Wood, R. H. and DeLaney, D. E. *J. Phys. Chem.* 72 (1968) 4651.
- Kiss, G., Zhang, K., Mukerjee, S. L., Hoff, C. D. and Roper, G. C. *J. Am. Chem. Soc.* 112 (1990) 5657.
- Peters, D. G. In: Lund, H. and Baizer, M. M., Eds., *Organic Electrochemistry, and Introduction and Guide*, Dekker, New York 1991, Chap. 8 and references cited therein.

Received September 2, 1991.