

Estimation of Standard Reduction Potentials of Halogen Atoms and Alkyl Halides

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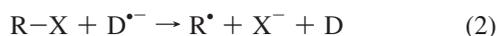
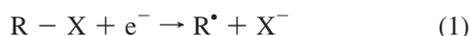
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Standard reduction potentials, SRPs, of the halogen atoms have been calculated in water on the basis of an appropriate thermochemical cycle. Using the best up-to-date thermodynamic data available in the literature, we have calculated $E_{X^{\bullet}/X^-}^{\circ}$ values of 3.66, 2.59, 2.04, and 1.37 V vs SHE for F[•], Cl[•], Br[•], and I[•], respectively. Additionally, we have computed the SRPs of Cl[•], Br[•], and I[•] in acetonitrile (CH₃CN) and dimethylformamide (DMF) by correcting the values obtained in water for the free energies of transfer of X[•] and X⁻ from water to the nonaqueous solvent S and the intersolvent potential between water and S. From the values of $E_{X^{\bullet}/X^-}^{\circ}$ in CH₃CN and DMF, the SRPs of a series of alkyl halides of relevance to atom transfer radical polymerization and other important processes such as pollution abatement have been calculated in these two solvents. This has been done with the aid of a thermochemical cycle involving the gas-phase homolytic dissociation of the C–X bond, solvation of RX, R[•], and X[•], and reduction of X[•] to X⁻ in solution.

Introduction

Injection of a single electron into an organic halide often leads to the rupture of a carbon–halogen bond.¹ This process follows either a concerted mechanism in which electron transfer and bond breaking occur in a single step, or a stepwise mechanism involving the intermediate formation of a radical anion.^{1,2} Both homogeneous³ and heterogeneous^{4,5} reduction of most alkyl halides follows the concerted mechanism, which can be written as



where D^{•-} stands for a homogeneous donor, which might be an aromatic compound or a metal complex. Reductive cleavage of alkyl halides plays an important role in several important processes such as reductive dehalogenation of recalcitrant pollutants,^{6–8} atom transfer radical polymerization,⁹ and various other processes of synthetic importance.¹⁰ Reduction of alkyl halides has also attracted much interest as a model for the investigation of the mechanism and dynamics of dissociative electron-transfer processes.¹¹

Information on the kinetics and thermodynamics of the reductive cleavage of carbon–halogen bonds is important to the full comprehension of the mechanism of the above-mentioned processes; these data are also useful in the optimization of synthetic and catalytic processes. The standard reduction potentials, SRPs, of alkyl halides undergoing concerted dissociative electron transfer (eq 1) cannot be experimentally measured. In fact, an irreversible reduction peak (or wave) occurring at potentials that are considerably more negative than the standard potential, $E_{RX/R^{\bullet}+X^-}^{\circ}$, is observed because of the

sluggishness of the electron transfer. However, $E_{RX/R^{\bullet}+X^-}^{\circ}$ may be calculated if one incorporates reaction 1 into a thermochemical cycle involving reactions with known thermodynamic data.^{4a,12} The most simple thermochemical cycle, which is also the most widely used one, involves homolytic dissociation of the C–X bond followed by 1e⁻ reduction of X[•] to X⁻. Therefore, estimation of $E_{RX/R^{\bullet}+X^-}^{\circ}$ requires knowledge of the RX bond dissociation energy, BDE, and the standard potential of the X[•]/X⁻ couple. Although BDE values are available in the literature for a large number of alkyl halides,¹³ only a few contrasting values have been reported for $E_{X^{\bullet}/X^-}^{\circ}$.^{4c,14}

The aim of this paper is to calculate the standard reduction potentials of the halogen atoms in water as well as in two popular organic solvents, namely, acetonitrile and dimethylformamide. From an appropriate thermochemical cycle, $E_{X^{\bullet}/X^-}^{\circ}$ in water will be first calculated on the basis of the most up-to-date available thermodynamic data. The ensuing values will then be used to calculate $E_{X^{\bullet}/X^-}^{\circ}$ in nonaqueous solvents. The second objective of the paper is to critically examine the commonly used method of calculation of SRPs of alkyl halides in aprotic solvents and to apply it for the calculation of $E_{RX/R^{\bullet}+X^-}^{\circ}$ of a series of important alkyl halides.

Computational Methods

Free energies of solvation for the studied species in water, acetonitrile, and dimethylformamide were calculated from the conductor-like polarizable continuum model, CPCM, the universal solvation model based on solute electron density, SMD, and conductor like screening model for realistic solvents, COSMO-RS.¹⁵ CPCM¹⁶ and SMD¹⁷ calculations were performed in Gaussian 03 and 09, respectively,¹⁸ whereas COSMO-RS calculations were performed in ADF.¹⁹

These calculations were carried out with theoretical procedures for which they were parametrized, namely, HF/6-31+G(d) with UAHF radii for CPCM, HF/6-31G(d) for SMD and BP/TZVP for COSMO-RS, all geometries being optimized at the same level. For species containing third-row atoms, Br and Kr, we adopted Rassolov's 6-31G²⁰ rather than the default

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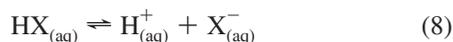
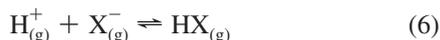
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version in Gaussian. Rassolov's 6-31G basis set is consistent with first- and second-row atoms, whereas the default Gaussian 6-31G basis set is not. For species containing fourth-row atoms, I and Xe, LACVP+* was used instead of 6-31+G*. For Xe, the extra diffuse function is unavailable and unnecessary; therefore only polarization was applied.

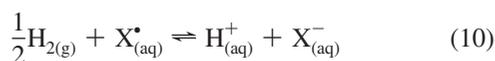
The calculated free energy of solvation can be expressed as the sum of the energy required to create a cavity in the solvent for the solute molecule, ΔG_{cav} , and the solute-solvent interactions, which can be decomposed into electrostatic, ΔG_{elst} , dispersion, ΔG_{disp} , and repulsion, ΔG_{rep} , contributions. Thus, $\Delta G_{\text{sol}} = \Delta G_{\text{elst}} + \Delta G_{\text{disp}} + \Delta G_{\text{rep}} + \Delta G_{\text{cav}}$. For Xe, the contributions from ΔG_{disp} and ΔG_{rep} were neglected from the program. We have applied extrapolation functions on the noble gas series in order to get these two terms. The free energy of each species in solution was then obtained as the sum of the corresponding gas-phase free energy, the calculated free energy of solvation, and a correction term, $RT \ln(V^\ominus)$, to take account of the fact that the standard solvation energy is referred to the passage from 1 atm (ideal gas) to 1 mol L⁻¹ (standard solution),²¹ whereas ΔG_{sol} is calculated for the passage from an ideal gas at 1 mol L⁻¹ to 1 mol L⁻¹ standard solution.

Results and Discussion

Thermodynamics of reduction of X[•] to X⁻. The value of $E_{\text{X}^\bullet/\text{X}^-}^\ominus$ in water can be computed according to the following thermodynamic cycle, in which each species is considered in its proper standard state:



The overall process is

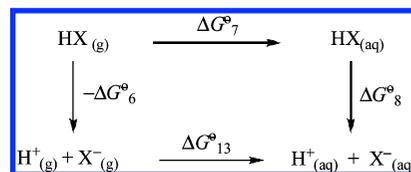


and

$$\Delta G_{10}^\ominus = \Delta G_3^\ominus + \Delta G_4^\ominus + \Delta G_5^\ominus + \Delta G_6^\ominus + \Delta G_7^\ominus + \Delta G_8^\ominus + \Delta G_9^\ominus = -FE_{\text{X}^\bullet/\text{X}^-}^\ominus \text{ vs SHE} \quad (11)$$

$E_{\text{X}^\bullet/\text{X}^-}^\ominus$ values calculated with this thermochemical cycle have already been reported in the literature.^{14a,22} We wish to improve these data by using the most up-to-date available thermodynamic

SCHEME 1



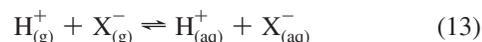
data²³ and also by correcting some assumptions made in the previous estimations. We have estimated the Gibbs free energies of the above reactions as follows. The free energy of the gas-phase electron capture by X[•] can be calculated as

$$\Delta G_3^\ominus = \Delta H_3^\ominus - T(S_{\text{X}^-}^\ominus - S_{\text{X}^\bullet}^\ominus - S_{\text{e}^-}^\ominus) = -EA - (H_{\text{e}^-}^\ominus - H_{\text{X}^\bullet}^\ominus) - T(S_{\text{X}^-}^\ominus - S_{\text{X}^\bullet}^\ominus - S_{\text{e}^-}^\ominus) \quad (12)$$

where EA is the electron affinity of X[•] at 0 K. To calculate ΔH_3^\ominus we start from EA and compute the integrated heat capacities of X[•], X⁻, and e⁻. The integrated heat capacity of the electron at 298.15 K, $H_{\text{e}^-}^\ominus$, is 3.145 kJ mol⁻¹ and $H_{\text{e}^-}^0$ is 0 kJ mol⁻¹,²⁴ whereas assuming X[•] and X⁻ to behave as ideal monatomic gases, the difference between their integrated heat capacities (each about $^{5/2}RT$) can be neglected. The entropies of X[•], X⁻, and e⁻ are available in the literature²³ and, in particular, $S_{\text{e}^-}^\ominus = 22.734 \text{ J mol}^{-1}\text{K}^{-1}$, according to the electron convention Fermi-Dirac statistics.²⁴

Reaction 4 is the homolytic dissociation of H₂ with $\Delta G_4^\ominus = 203.25 \text{ kJ mol}^{-1}$.²⁴ Also the ionization free energy, ΔG_5^\ominus , of H[•] has been reported to be 1310.075 kJ mol⁻¹.²⁴ The Gibbs free energy of reaction 6 can be calculated as $\Delta G_6^\ominus = \Delta H_6^\ominus - T(S_{\text{HX}}^\ominus - S_{\text{X}^-}^\ominus - S_{\text{H}^+}^\ominus) = -PA - T(S_{\text{HX}}^\ominus - S_{\text{X}^-}^\ominus - S_{\text{H}^+}^\ominus)$, where PA is the gas phase proton affinity of X⁻.

Experimental data for the hydration free energy of HX, ΔG_7^\ominus , are not available in the literature. Apart from HF, these compounds are very strong acids that undergo complete dissociation in water, which makes the accurate measurement of the solubility of HX and hence its hydration free energy impossible. ΔG_7^\ominus can be calculated by combination of reactions 6 and 8 with the hydration of H⁺ and X⁻ (eq 13), according to the thermochemical cycle shown in Scheme 1.



The free energy of reaction 8 is related to the pK_a of HX as $\Delta G_8^\ominus = -RT \ln K_a = 2.303RTpK_a$, whereas ΔG_{13}^\ominus is the conventional hydration free energy of X⁻, $\Delta_c G_{\text{aq}}^\ominus(\text{X}^-)$, taking $\Delta_c G_{\text{aq}}^\ominus(\text{H}^+) = 0$ by convention.²⁵ Therefore, if pK_a is known, the hydration free energy of HX can be easily calculated as

$$\Delta G_7^\ominus = \Delta G_{\text{aq}}^\ominus(\text{HX}) = \Delta G_{13}^\ominus - \Delta G_6^\ominus - 2.303RTpK_a \quad (14)$$

Unfortunately, reliable values of pK_a are not available, except for HF, because they are too small (pK_a < -7) to be experimentally measured with acceptable accuracy in water. Several estimations based on thermochemical cycles involving hydration of HX have been reported, but the pK_a values obtained for each HX show great variations, reaching several orders of magnitude, mainly due to the different values adopted for $\Delta G_{\text{aq}}^\ominus(\text{HX})$.^{22a,26} Although, at the moment, the separate values of ΔG_7^\ominus and ΔG_8^\ominus cannot be obtained, eq 14 provides the sum

of their values as $\Delta G_7^\circ + \Delta G_8^\circ = \Delta G_{13}^\circ - \Delta G_6^\circ$ and this suffices for our purpose. Since both ΔG_{13}° and ΔG_6° are available, their difference can be substituted in eq 11 for the sum of ΔG_7° and ΔG_8° .

To sum up, the free energy of the redox reaction 10 can be expressed by the following simplified equation:

$$\Delta G_{10}^\ominus = \Delta G_3^\ominus + \Delta G_4^\ominus + \Delta G_5^\ominus + \Delta G_9^\ominus + \Delta G_{13}^\ominus = -EA - T(S_{X^-}^\ominus - S_{X^\cdot}^\ominus) + \Delta G_9^\ominus - \Delta G_{13}^\ominus + 1516.958 \text{ kJ mol}^{-1} \quad (15)$$

where the numeric term arises from the sum: $\Delta G_4^\ominus + \Delta G_5^\ominus - (H_{e^-}^\ominus - H_{c^-}^\ominus) + TS_{e^-}^\ominus$.

Gibbs Free Energy of X[•] Solvation. All parameters of eq 15 are known except the free energy of hydration of the halogen atoms, $\Delta G_9^\ominus = -\Delta G_{\text{aq}}^\ominus(X^\cdot)$, for which experimental data are not available in the literature. As suggested by Ritchie,^{22b} one way to estimate $\Delta G_{\text{aq}}^\ominus(X^\cdot)$ is to assume it to be approximately equal to $\Delta G_{\text{aq}}^\ominus(\text{HX})$, which means $\Delta G_7^\ominus \approx -\Delta G_9^\ominus$ and hence their contributions cancel out in eq 11. This assumption, however, does not completely resolve the problem because, if we substitute $-\Delta G_9^\ominus$ for ΔG_7^\ominus in eq 11, we are then left with ΔG_8^\ominus which is unknown. Furthermore, assuming similar hydration behavior for X[•] and HX, which has a polar bond and is able to form hydrogen bonds, is questionable. A better approximation has been proposed by Pearson,^{22a} who suggests the use of $\Delta G_{\text{aq}}^\ominus(\text{CH}_3\text{X})$, which can be calculated from solubility data,²⁷ as an estimate of $\Delta G_{\text{aq}}^\ominus(X^\cdot)$. We believe, however, that this approximation also gives only very rough estimates, considering that CH₃X has a polar bond and is significantly bigger than X[•].

Another reasonable approximation, which has been used for the estimation of the solvation free energy of atomic radicals,²⁸ is to assume that the mechanism of solvation of atomic species such as X[•] in water is the same as that of the noble gases. It has been shown that $\Delta G_{\text{aq}}^\ominus$ of rare gases varies linearly with the van der Waals radius, *r*, of the atom.²⁹ Regression analysis of hydration free energies of the noble gases He, Ne, Ar, Kr, and Xe in water as a function of *r* in Å gives the equation³⁰

$$\Delta G_{\text{aq}}^\ominus (\text{kJ mol}^{-1}) = 31.15 - 8.06r \quad (16)$$

with a correlation coefficient $R^2 = 0.98$.

To examine if any of these approximate methods gives acceptable $\Delta G_{\text{aq}}^\ominus(X^\cdot)$ values, we conducted a small computational study in which the $\Delta G_{\text{aq}}^\ominus(X^\cdot)$ values were computed directly by means of three different popular computational methods. Using the same procedures, we also computed the $\Delta G_{\text{aq}}^\ominus(\text{HX})$, $\Delta G_{\text{aq}}^\ominus(\text{CH}_3\text{X})$, $\Delta G_{\text{aq}}^\ominus(\text{X}+1)$, and $\Delta_c G_{\text{aq}}^\ominus(\text{X}^-)$ and, where possible, compared them with experiment. The noble-gas solvation energies, $\Delta G_{\text{aq}}^\ominus(\text{X}+1)$, were used to obtain estimates of $\Delta G_{\text{aq}}^\ominus(X^\cdot)$ values via eq 16. All results are listed in Table 1, from which it is clear that none of the approximate methods reproduce the corresponding X[•] solvation energy; $\Delta G_{\text{aq}}^\ominus(\text{CH}_3\text{X})$ underestimates the $\Delta G_{\text{aq}}^\ominus(X^\cdot)$ values, Eq 16 overestimates the values, and $\Delta G_{\text{aq}}^\ominus(\text{HX})$ gives diametrically opposed trends. It is therefore clear that use of these approximations, in place of the actual $\Delta G_{\text{aq}}^\ominus(X^\cdot)$ values, introduces an additional source of error that should be avoided. For this reason we have opted to use theoretical $\Delta G_{\text{aq}}^\ominus(X^\cdot)$ values for the present work. To choose a suitable level of theory, we can compare

TABLE 1: Assessment Study of Gibbs Free Energies (kJ mol⁻¹) of Solvation of the Halogen Atoms, HX, CH₃X, Noble Gases and Halide Anions Using Different Methods

	radical (X [•])	HX	CH ₃ X	noble gas (X + 1)	Anion (X ⁻)
CPCM					
F	12.44	-19.38	5.26	18.78	-419.45
Cl	13.11	5.52	5.01	15.85	-299.16
Br	10.85	7.11	3.97	14.18	-279.00
I	9.89	11.33	4.18	12.67 ^a	-248.83
SMD					
F	13.55	-11.51	6.06	7.90	-380.54
Cl	8.28	-0.30	2.59	7.82	-274.81
Br	4.59	4.72	2.13	7.77	-218.08
I	-5.24	-3.90	0.75	7.61	-261.80
COSMO-RS					
F	-8.12	-15.18	9.36	16.47	-497.94
Cl	-5.97	3.64	4.59	-0.46	-304.99
Br	14.96	14.54	13.11	12.36	-255.50
I	21.28	13.51	15.43	10.37	-220.92
eq 16^b					
F	19.30				
Cl	17.04				
Br	16.40				
I	15.19				
exp					
F		-23.77 ^c	7.38 ^d	19.06 ^e	-432.7 ^f
Cl			5.95 ^d	16.25 ^e	-307.6 ^f
Br			4.99 ^d	14.83 ^e	-281.3 ^f
I			4.93 ^d	13.45 ^e	-246.2 ^f
MAD^g					
CPCM			1.21	0.53	6.65
SMD			2.93	8.12	40.94
COSMO-RS			5.49	6.21	29.73

^a Dispersion (-27.97 kJ mol⁻¹) and repulsion (3.73 kJ mol⁻¹) energies are calculated from extrapolation of the values of Ne, Ar and Kr. ^b Van der Waals radii for F, Cl, Br, and I are 1.47, 1.75, 1.83, and 1.98 (Å) respectively, from ref 30b. ^c Taken from ref 23. ^d Taken from ref 22a. ^e Experimental values taken from ref 29 were corrected for the change of solution standard state from $x_{\text{solute}} = 1$ to $C_{\text{solute}} = 1 \text{ M}$ (see ref 30a for more details). ^f Calculated by subtracting the hydration free energy of the proton ($\Delta G_{\text{aq}}^\ominus(\text{H}^+) = -1100.9 \text{ kJ mol}^{-1}$)^{33b} from the conventional hydration free energies reported in ref 25 for X⁻. ^g Overall MAD values are 2.80, 17.33, and 13.81 kJ mol⁻¹ for CPCM, SMD, and COSMO-RS, respectively.

the theoretical values for CH₃X, X⁻, and the noble gases with the available experimental data. Examining Table 1, we note that CPCM reproduces the experimental data to within chemical accuracy, whereas the other methods show significantly larger deviations. The mean absolute error of CPCM over the whole set of data for CH₃X, X⁻ and noble gases is 2.80 kJ mol⁻¹, which can be compared with 16.35 for SMD and 13.81 for COSMO-RS. As expected, for all methods the errors are greatest for charged species, which are generally known to be more difficult to model theoretically. It should be stressed that, in the present determination of E_{X^\cdot/X^-}^\ominus and $E_{R^\cdot/R^-}^\ominus + X^-$, experimental solvation energies are used for the X⁻ anions; computed CPCM solvation energies are used only for the neutral species.

Calculation of E^o_{X[•]/X⁻} in a Solvent S. The standard reduction potential, SRP, of X[•] in water is defined as $E_{X^\cdot/X^-}^\ominus = -\Delta G_{10}^\ominus/ F$, where $-\Delta G_{10}^\ominus$ is given by eq 15. The thermodynamic data required for the calculation of ΔG_{10}^\ominus from eq 15 are listed in Table 2. The table also reports values of E_{X^\cdot/X^-}^\ominus in water calculated from the obtained ΔG_{10}^\ominus values. These SRPs compare well with literature data estimated from different thermochemical cycles.^{14b,31} Our results are, on average, about 0.08 V more positive than previous estimations by Savéant,^{14b} the difference

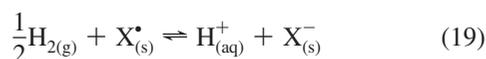
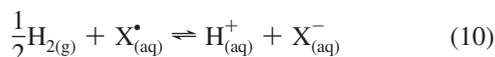
TABLE 2: Gibbs Free Energies (kJ mol⁻¹) of the Reactions Used for the Calculation of the Standard Potentials of Halogen Atoms in Water at 298.15 K

	process	F	Cl	Br	I
(3)	$X_{(g)}^{\bullet} + e^{-} \rightleftharpoons X_{(g)}^{-}$	-320.60 ^a	-341.58 ^a	-317.46 ^a	-288.08 ^a
(4)	$\frac{1}{2}H_{2(g)} \rightleftharpoons H_{(g)}^{\bullet}$	203.25 ^b	203.25	203.25	203.25
(5)	$H_{(g)}^{\bullet} \rightleftharpoons H_{(g)}^{+} + e^{-}$	1310.08 ^c	1310.08	1310.08	1310.08
(13)	$H_{(g)}^{+} + X_{(g)}^{-} \rightleftharpoons H_{(aq)}^{+} + X_{(aq)}^{-}$	-1533.6 ^d	-1408.5 ^d	-1382.2 ^d	-1347.1 ^d
(9)	$X_{(aq)}^{\bullet} \rightleftharpoons X_{(g)}^{\bullet}$	-12.44 ^e	-13.11 ^e	-10.85 ^e	-9.89 ^e
(10)	$X_{(aq)}^{\bullet} + \frac{1}{2}H_{2(g)} \rightleftharpoons H_{(aq)}^{+} + X_{(aq)}^{-}$	-353.30	-249.86	-197.19	-131.74
	$E_{X^{\bullet}/X^{-}}^{\ominus}$ (V vs SHE)	3.66	2.59	2.04	1.37

^a Calculated from eq 12, using data taken from ref 23. ^b Taken from ref 23. ^c Taken from ref 24. ^d Taken from ref 25. ^e Computed according to CPCM.

principally arising from the rough approximations made in estimating $\Delta G_{aq}^{\circ}(X^{\bullet})$ in the previous calculations of SRP.

Starting from the value of $E_{X^{\bullet}/X^{-}}^{\circ}$ in water, one can estimate the SRP of X^{\bullet} in any solvent S by considering the following thermochemical cycle:

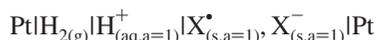


The Gibbs free energy of reaction 19 is given by

$$\Delta G_{19}^{\ominus} = \Delta G_{10}^{\ominus} - \Delta_{tr}G_{X^{\bullet}}^{\ominus, aq \rightarrow s} + \Delta_{tr}G_{X^{-}}^{\ominus, aq \rightarrow s} \quad (20)$$

where $\Delta_{tr}G_X^{\ominus, aq \rightarrow s}$ is the free energy of transfer of the species X from water to the solvent S. The free energies of transfer of the halide ions are known for many organic solvents.³² The free energy of reaction 17 can be calculated as the difference between the Gibbs energies of solvation of X^{\bullet} in water and in the solvent S, $\Delta_{tr}G_{X^{\bullet}}^{\ominus, aq \rightarrow s} = \Delta G_s^{\circ}(X^{\bullet}) - \Delta G_{aq}^{\circ}(X^{\bullet})$.

Once we calculate the free energy of reaction 19, we can express it as a redox potential by considering the following cell:



Taking into consideration the existence of an intersolvent potential, E_L , between the two half cells, the SRP of X^{\bullet} is given by

$$E_{X^{\bullet}/X^{-},s}^{\ominus, SHE, aq} = -\frac{\Delta G_{19}^{\ominus}}{F} + E_L = E_{X^{\bullet}/X^{-},aq}^{\ominus, SHE, aq} + \frac{1}{F}(\Delta_{tr}G_{X^{\bullet}}^{\ominus, aq \rightarrow s} - \Delta_{tr}G_{X^{-}}^{\ominus, aq \rightarrow s}) + E_L \quad (21)$$

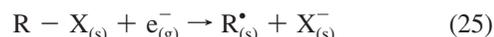
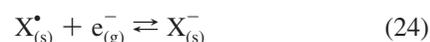
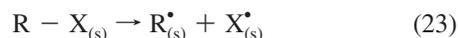
where $\Delta G_{19}^{\ominus} = \Delta G_{10}^{\ominus} - \Delta_{tr}G_{X^{\bullet}}^{\ominus, aq \rightarrow s} + \Delta_{tr}G_{X^{-}}^{\ominus, aq \rightarrow s}$ and $\Delta G_{10}^{\ominus} = -FE_{X^{\bullet}/X^{-},aq}^{\ominus, SHE, aq}$. We use the notation $E_{X^{\bullet}/X^{-},s}^{\ominus, SHE, aq}$ to indicate the standard

reduction potential of the X^{\bullet}/X^{-} couple in the solvent S vs the aqueous standard hydrogen electrode. Conversion of $-FE_{X^{\bullet}/X^{-},s}^{\ominus, SHE, aq}$ to the aqueous SCE scale gives

$$E_{X^{\bullet}/X^{-},s}^{\ominus, SCE, aq} = E_{X^{\bullet}/X^{-},aq}^{\ominus, SHE, aq} + \frac{1}{F}(\Delta_{tr}G_{X^{\bullet}}^{\ominus, aq \rightarrow s} - \Delta_{tr}G_{X^{-}}^{\ominus, aq \rightarrow s}) + E_L - 0.241 \quad (22)$$

Table 3 reports the free energies of transfer of X^{\bullet} and X^{-} from water to MeCN and DMF, together with the SRPs calculated from eq 22. The values of E_L used in eq 22 are 0.093 and 0.172 V for MeCN and DMF, respectively.³³ Several compilations of $\Delta_{tr}G_{X^{\bullet}}^{\ominus, aq \rightarrow s}$ from water to many organic solvents are available in the literature.³² In particular, reviews by Gritzner^{32a} and Marcus et al.^{32c} give similar $\Delta_{tr}G_{X^{\bullet}}^{\ominus, aq \rightarrow s}$ values for the transfer of halide ions from water to MeCN and DMF. On the average, the values of $\Delta_{tr}G_{X^{\bullet}}^{\ominus, aq \rightarrow s}$ reported by Gritzner differ from those of Marcus et al. by 1.4 kJmol⁻¹, except in the case of transfer of Br⁻ from water to DMF, where the difference is 6.1 kJmol⁻¹. Here, we used data from the most recent compilation by Gritzner.^{32a} However, even if one uses other $\Delta_{tr}G_{X^{\bullet}}^{\ominus, aq \rightarrow s}$ data, calculated SRPs would be equal to those reported in Table 3 to within ca 0.02 V, except in the case of Br⁻ in DMF, which would give a SRP of 1.69 instead of 1.75 V vs SCE.

Calculation of $E_{RX/R^{\bullet}+X^{-}}^{\circ}$. The SRP of any species undergoing concerted dissociative electron transfer in a solvent S can be obtained through a thermochemical cycle such as the following one for RX:

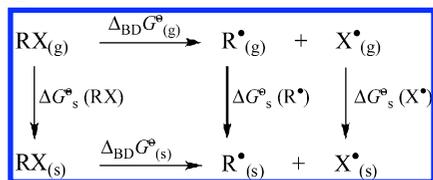


The standard reduction potential of reaction 25, $E_{RX/R^{\bullet}+X^{-}}^{\circ}$, can be calculated as the sum of the Gibbs free energies of reactions 23 and 24.^{1b} The free energy of reaction 23 can be estimated starting from the free energy of the same reaction in the gas phase, according to the thermochemical cycle shown in Scheme 2, where $\Delta_{BD}G^{\circ}$ is the Gibbs free energy of R-X bond

TABLE 3: Standard Reduction Potentials of the Halogen Atoms at 298.15 K

X ⁻	H ₂ O	acetonitrile			dimethylformamide				
	$E_{X^{\ominus}/X^-}^{\ominus}$, V vs SHE	$\Delta_{tr}G_X^{\ominus, aq^{-s}, a}$ kJ mol ⁻¹	$\Delta G_s^{\ominus}(X^{\bullet}),^b$ kJ mol ⁻¹	$\Delta_{tr}G_X^{\ominus, aq^{-s}, c}$ kJ mol ⁻¹	$E_{X^{\ominus}/X^-}^{\ominus}$, V vs SCE	$\Delta_{tr}G_X^{\ominus, aq^{-s}, a}$ kJ mol ⁻¹	$\Delta G_s^{\ominus}(X^{\bullet}),^b$ kJ mol ⁻¹	$\Delta_{tr}G_X^{\ominus, aq^{-s}, c}$ kJ mol ⁻¹	$E_{X^{\ominus}/X^-}^{\ominus}$, V vs SCE
F	3.66	45.0 ^d	14.03	1.59	3.06	51 ^e	17.92	5.48	3.12
Cl	2.59	41.7	15.28	2.17	2.03	46.0	20.81	7.70	2.12
Br	2.04	31.4	13.86	3.01	1.60	30.1	19.47	8.62	1.75
I	1.37	19.4	13.48	3.59	1.06	18.8	19.80	9.91	1.21

^a Unless otherwise noted, data are from ref 32a. ^b Computed according to CPCM. ^c Calculated as $\Delta_{tr}G_X^{\ominus, aq^{-s}} = \Delta G_s^{\ominus}(X^{\bullet}) - \Delta G_{aq}^{\ominus}(X^{\bullet})$. ^d Taken from ref 32b. ^e Taken from ref 32c.

SCHEME 2

dissociation and ΔG_s^{\ominus} is the Gibbs free energy of solvation in the solvent S.

Taking into account the solvation free energies of RX, R[•], and X[•], the free energy of reaction 25 can be expressed as

$$\Delta G_{25}^{\ominus} = \text{BDE} - T\Delta_{\text{BD}}S_{(g)}^{\ominus} + \Delta G_s^{\ominus}(R^{\bullet}) + \Delta G_s^{\ominus}(X^{\bullet}) - \Delta G_s^{\ominus}(RX) - FE_{X^{\ominus}/X^-}^{\ominus} \quad (26)$$

where BDE and $\Delta_{\text{BD}}S_{(g)}^{\ominus}$ are the bond dissociation enthalpy and entropy in the gas phase. Thus, SRP of RX is given by

$$E_{\text{RX}/\text{R}^{\bullet}+\text{X}^{\bullet}}^{\ominus} = \frac{1}{F}(-\text{BDE} + T\Delta_{\text{BD}}S_{(g)}^{\ominus} - \Delta\Delta G_s^{\ominus}) + E_{X^{\ominus}/X^-}^{\ominus} \quad (27)$$

where $\Delta\Delta G_s^{\ominus} = \Delta G_s^{\ominus}(R^{\bullet}) + \Delta G_s^{\ominus}(X^{\bullet}) - \Delta G_s^{\ominus}(RX)$. The difference between the solvation free energies of the reagents and products is often assumed to be negligible. This assumption is mainly based on observations that bond energies of various compounds, in particular C–H bonds, have similar values in the gas phase and in nonpolar solvents.³⁴ Experimental data for the free energy of the homolytic dissociation, $\Delta_{\text{BD}}G_{(s)}^{\ominus}$, of carbon–halogen bonds in solution are not available for comparison with known gas-phase values. Recently, some of us³⁵ have reported theoretical calculations on thermodynamic properties of an extended series of organic halides of relevance to atom transfer radical polymerization, showing that the C–X bond dissociation energy is little affected by polar solvents such as acetonitrile and dimethylformamide, though on the average $\Delta_{\text{BD}}G_{(s)}^{\ominus}$ decreases in these solvents. Thus, in the absence of precise values of $\Delta_{\text{BD}}G_{(s)}^{\ominus}$, only the gas-phase bond energies may be used for the estimation of $E_{\text{RX}/\text{R}^{\bullet}+\text{X}^{\bullet}}^{\ominus}$, neglecting the contribution of $\Delta\Delta G_s^{\ominus}$ in eq 27. This is exactly what has been done so far in most literature estimations of $E_{\text{RX}/\text{R}^{\bullet}+\text{X}^{\bullet}}^{\ominus}$. We believe that a better approximation is to use average $\Delta\Delta G_s^{\ominus}$ values that can be evaluated from the data reported in our previous paper on the high-level *ab initio* computation of C–X bond energies. In fact, that paper reports $\Delta_{\text{BD}}G_{(g)}^{\ominus}$ and $\Delta_{\text{BD}}G_{(s)}^{\ominus}$ for various alkyl halides and, according to Scheme 2, the difference between these free energies gives $\Delta\Delta G_s^{\ominus}$

$$\Delta\Delta G_s^{\ominus} = \Delta G_s^{\ominus}(R^{\bullet}) + \Delta G_s^{\ominus}(X^{\bullet}) - \Delta G_s^{\ominus}(RX) = \Delta_{\text{BD}}G_{(s)}^{\ominus} - \Delta_{\text{BD}}G_{(g)}^{\ominus} \quad (28)$$

Considering a series of each type of alkyl halide, the following average $\Delta\Delta G_s^{\ominus}$ values were obtained for RCl, RBr, and RI, respectively: 0.43, –1.0, and –2.1 kJ mol⁻¹ in DMF and –2.56, –3.77, and –4.95 kJ mol⁻¹ in MeCN.

Using the above average $\Delta\Delta G_s^{\ominus}$ values, we have calculated from eq 27 the SRPs of an extended series of alkyl halides in DMF and MeCN. The selected compounds contain activated alkyl halides, simple unsubstituted haloalkanes, and volatile polyhalomethanes. Reduction of these compounds is extensively investigated for various reasons. Reduction of polyhalomethanes both at metals such as iron and at catalytic electrodes is widely studied as a reductive destruction method for the abatement of water pollutants.^{6–8} Several activated alkyl halides such as haloacetonitriles, methyl 2-halopropionates, 2-halopropionitriles, and benzyl halides are widely used as activators in atom transfer radical polymerization (ATRP);⁹ such compounds are also considered to be good mimics of the dormant species formed during polymerization of various monomers such as acrylonitrile, acrylates, and styrenes. Last, the redox properties of both activated and simple unsubstituted haloalkanes are important because such compounds have played a fundamental role in the development of the dissociative electron-transfer theory.^{2,4,5}

Experimental values of BDE are reported for many of the selected compounds, especially simple alkyl halides without activating substituents, polyhalomethanes, and benzyl halides.^{13,36–38} However, no experimental data are available for activated alkyl halides bearing functional groups such as cyanides and esters. Instead, theoretically computed data based on high-level *ab initio* molecular orbital calculations have recently been reported for various activated alkyl halides.³⁵ Where experimental data were not available, we used the computed BDE values reported in the above paper.

To use eq 28 for the calculation of $E_{\text{RX}/\text{R}^{\bullet}+\text{X}^{\bullet}}^{\ominus}$, one also needs the gas-phase bond dissociation entropy, $\Delta_{\text{BD}}S_{(g)}^{\ominus}$, for which there are no experimental data, whereas theoretically computed values are reported for most of the selected compounds. Therefore, when available, we used the theoretical $\Delta_{\text{BD}}S_{(g)}^{\ominus}$ values. When, however, no literature data were available at all, we used the average of the $\Delta_{\text{BD}}S_{(g)}^{\ominus}$ values reported by Lin et al.³⁵ for each type of halogen atom. These are 38.8, 37.8, and 37.7 J mol⁻¹K⁻¹ for RCl, RBr, and RI, respectively.

The standard reduction potentials calculated for a series of alkyl halides in MeCN and DMF are reported in Table 4. The table also reports (columns 5 and 7) the values of $\Delta\Delta G_s^{\ominus}$ used for the calculation of the SRPs, which were obtained as the difference between theoretically computed values of $\Delta_{\text{BD}}G_{(g)}^{\ominus}$ and $\Delta_{\text{BD}}G_{(s)}^{\ominus}$. We report in the last column literature data on $E_{\text{RX}/\text{R}^{\bullet}+\text{X}^{\bullet}}^{\ominus}$ in DMF.^{4,35–37,39} It is to be stressed that experimentally measured SRPs do not exist for these compounds, so the

TABLE 4: Standard Reduction Potentials of Alkyl Halides in MeCN and DMF at 298.15 K

entry	RX	BDE, ^a kJ mol ⁻¹	TΔS [⊖] , ^b kJ mol ⁻¹	this work				literature E [⊖] _{RX/R'+X⁻} , V vs SCE
				MeCN		DMF		
				ΔΔG [⊖] , ^b kJ mol ⁻¹	E [⊖] _{RX/R'+X⁻} , V vs SCE	ΔΔG [⊖] , ^b kJ mol ⁻¹	E [⊖] _{RX/R'+X⁻} , V vs SCE	
1	CCl ₄	298.0 ^c	37.5 ^c	-2.56 ^d	-0.64	0.43 ^d	-0.58	-0.58 ^g ; -0.65 ^e ; -0.72 ^f
2	CHCl ₃	318.0 ^c	32.6 ^c	-2.56 ^d	-0.90	0.43 ^d	-0.84	-0.84 ^c
3	CH ₂ Cl ₂	335.0 ^c	30.3 ^c	-2.56 ^d	-1.10	0.43 ^d	-1.04	-1.04 ^c
4	CH ₃ CH ₂ Cl	352.3 ^c	38.8 ^d	-2.56 ^d	-1.19	0.43 ^d	-1.13	
5	NCCH ₂ Cl	299.5 ^g	36.1	2.22	-0.72	6.36	-0.68	-0.52 ^g ; -0.96 ^h
6	EtO ₂ CCH ₂ Cl	320.8 ^g	41.9	-2.59	-0.83	0.33	-0.77	-0.61 ^g
7	CH ₃ CH(Cl)CN	301.9 ^g	38.8	-5.44	-0.64	-2.47	-0.58	-0.42 ^g
8	MeO ₂ CCH(CH ₃)Cl	316.7 ^g	35.3	-3.89	-0.85	-1.21	-0.78	-0.62 ^g
9	<i>n</i> -C ₄ H ₉ Cl	350.6	38.8 ^d	-2.56 ^d	-1.18	0.43 ^d	-1.12	-1.29 ^f ; -1.36 ⁱ
10	<i>s</i> -C ₄ H ₉ Cl	350.2	38.8 ^d	-2.56 ^d	-1.17	0.43 ^d	-1.11	-1.37 ^f ; -1.37 ⁱ
11	<i>tert</i> -C ₄ H ₉ Cl	351.9	38.8 ^d	-2.56 ^d	-1.19	0.43 ^d	-1.13	-1.31 ^f ; -1.25 ⁱ
12	MeO ₂ CC(CH ₃) ₂ Cl	315.1 ^g	36.9	-3.89	-0.81	-0.63	-0.76	-0.60 ^g
13	EtO ₂ CC(CH ₃) ₂ Cl	315.8 ^g	42.1	-4.35	-0.76	-1.21	-0.70	-0.54 ^g
14	PhCH ₂ Cl	299.9 ^j	34.5	0.54	-0.73	3.51	-0.67	-0.60 ^g ; -0.70 ^f ; -0.76 ^k
15	PhCH(CH ₃)Cl	292.4 ^j	42.17	-1.55	-0.55	1.09	-0.48	-0.56 ^g
16	CBr ₄	242.3	37.8 ^l	-3.77 ^l	-0.48	-1.0 ^l	-0.36	
17	CHBr ₃	274.9	37.8 ^l	-3.77 ^l	-0.82	-1.0 ^l	-0.70	
18	CH ₃ CH ₂ Br	292.9	37.8 ^l	-3.77 ^l	-1.0	-1.0 ^l	-0.88	-1.14 ^f
19	BrCHClCH ₃	276.9 ^g	39.75	-2.72	-0.83	0.13	-0.71	-0.61 ^g
20	NCCH ₂ Br	246.3	35.6	1.21	-0.60	5.27	-0.49	-0.39 ^g ; -0.69 ^h
21	EtO ₂ CCH ₂ Br	267.6 ^g	34.8	-3.64	-0.78	-0.92	-0.65	-0.56 ^g
22	CH ₃ CH(Br)CN	246.5 ^g	38.4	-6.44	-0.49	-3.68	-0.37	-0.28 ^g
23	MeO ₂ CCH(CH ₃)Br	262.9 ^g	37.7	-5.19	-0.68	-2.80	-0.56	-0.46 ^g
24	<i>n</i> -C ₄ H ₉ Br	296.6	37.8 ^l	-3.77 ^l	-1.04	-1.0 ^l	-0.92	-1.14 ^f ; -1.22 ⁱ
25	<i>s</i> -C ₄ H ₉ Br	300.0	37.8 ^l	-3.77 ^l	-1.08	-1.0 ^l	-0.96	-1.21 ^f ; -1.21 ⁱ
26	<i>tert</i> -C ₄ H ₉ Br	292.9	37.8 ^l	-3.77 ^l	-1.0	-1.0 ^l	-0.88	-1.06 ^f ; -1.00 ⁱ
27	MeO ₂ CC(CH ₃) ₂ Br	258.4 ^g	37.3	-5.10	-0.64	-2.09	-0.52	-0.43 ^g
28	EtO ₂ CC(CH ₃) ₂ Br	259.0 ^g	42.7	-5.65	-0.58	-2.72	-0.46	-0.37 ^g
29	PhCH ₂ Br	239.3 ^j	34.8	-0.67	-0.51	2.05	-0.39	-0.47 ^g ; -0.63 ^k
30	PhCH(CH ₃)Br	240.1 ^j	35.49	-2.51	-0.49	-0.21	-0.37	-0.46 ^g
31	CH ₃ CH ₂ I	233.5	37.7 ^m	-4.95 ^m	-0.92	-2.1 ^m	-0.80	
32	NCCH ₂ I	179.1 ^h	35.0	1.12	-0.44	4.69	-0.33	-0.58 ^g ; -0.57 ^h
33	<i>tert</i> -C ₄ H ₉ I	227.2	37.7 ^m	-4.95 ^m	-0.85	-2.1 ^m	-0.73	-1.01 ^f ; -0.91 ⁱ
34	PhCH ₂ I	187.8 ^j	34.4	0.08	-0.53	0.33	-0.38	-0.62 ^g
35	PhCH(CH ₃)I	176.1 ^j	41.2	-0.42	-0.33	-1.76	-0.17	-0.54 ^g

^a Taken from ref 13, unless otherwise indicated. ^b Taken from ref 35, unless otherwise stated. ^c Taken from ref 36. ^d Average of the values reported for RCl in ref 35. ^e Taken from ref 4c. ^f Taken from ref 39. ^g Taken from ref 35. Note that *all* data taken from this reference are based on hindered rotor model (as used in Tables 1–2 of this reference) rather than the less accurate harmonic oscillator approximation (as used in Table 3). ^h Taken from ref 37. ⁱ Taken from ref 4a. ^j Taken from ref 38. ^k Taken from ref 4b. ^l Average of the values reported for RBr in ref 35. ^m Average of the values reported for RI in ref 35.

reported literature values are either estimates based on thermochemical cycles, often with some assumptions or theoretical computations. Although in some cases our $E_{\text{RX/R}'+\text{X}^-}^{\ominus}$ values significantly differ from those of previous estimations, overall the new set of data compares fairly well with the literature data. In particular, in the cases where the theoretical BDEs from ref 35 have been used in the present determinations of $E_{\text{RX/R}'+\text{X}^-}^{\ominus}$, the agreement with the theoretical values of $E_{\text{RX/R}'+\text{X}^-}^{\ominus}$ reported in this earlier study is, not surprisingly, very good. The minor discrepancies that do arise stem largely from differences between the experimental solvation energies of X⁻ used in the current values of $E_{\text{X}^{\ominus}/\text{X}^-}^{\ominus}$ compared with the calculated solvation energies used in the previous work. (A detailed analysis of these differences is provided in the Supporting Information.) As noted earlier, whereas the continuum solvation models used in the calculations generally reproduce the solvation energies of neutral molecules to within chemical accuracy, the errors tend to be larger for charged species. In essence, the present work is correcting the principal source of error in the previous computed values of $E_{\text{RX/R}'+\text{X}^-}^{\ominus}$ while still exploiting the demonstrated⁴⁰ ability of high-level ab initio molecular-orbital calculations to predict chemically accurate homolytic BDEs of neutral R–X compounds.

Conclusions

Standard reduction potentials of halogen atoms in water vs the standard hydrogen electrode have been calculated from the best up-to-date thermodynamic data available in the literature by means of a thermochemical cycle. Starting from the values of $E_{\text{X}^{\ominus}/\text{X}^-}^{\ominus}$ calculated for the redox reaction in water, we have also calculated the SRPs of X^{*} in MeCN and DMF vs SCE by considering the free energies of transfer of X^{*} and X⁻ from water to the nonaqueous solvent. In addition, a contribution due to the intersolvent potential between aqueous SCE and MeCN or DMF has been taken into account. Values of $E_{\text{X}^{\ominus}/\text{X}^-}^{\ominus}$ obtained in the nonaqueous solvents have been used to calculate the SRPs of a series of alkyl halides undergoing a concerted dissociative electron transfer. To this end, a thermochemical cycle involving gas-phase homolytic dissociation of the C–X bond, solvation of RX, R^{*}, and X^{*}, followed by reduction of X^{*} to X⁻ in the condensed phase has been considered.

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Supporting Information Available: Detailed comparison of our new $E_{\text{X}^{\ominus}/\text{X}^{\ominus}}$ values and the previous theoretical ones published in ref 35. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (30) (a) The Gibbs energies of hydration of the noble gases are reported for the following process: (1) solute (g, 1 atm) \rightarrow solute (aq, $x = 1$), whereas in our treatment we use a standard state of 1 M for the solute in solution. Therefore, we need ΔG° of the process: (2) solute (g, 1 atm) \rightarrow solute (aq, 1 M). The difference between the Gibbs free energies of these processes can be calculated by considering that $\Delta_1 G_{\text{aq}}^\circ = \mu_{\text{A, aq}} - \mu_{\text{A, g}} = \mu_{\text{A, aq}}^\circ - \mu_{\text{A, g}}^\circ$ and $\Delta_2 G_{\text{aq}}^\circ = \mu_{\text{A, aq}} - \mu_{\text{A, g}} = \mu_{\text{A, aq}}^\circ + RT \ln x_{\text{A}} - \mu_{\text{A, g}}^\circ$, where A stands for the solute and $\mu_{\text{A, aq}}^\circ$ is its standard chemical potential in an ideal dilute water solution obeying to Henry's law. For a 1 M solution the term $RT \ln x_{\text{A}}$ can be approximated to $RT \ln(1/55.6) = -9.96 \text{ kJ mol}^{-1}$, which leads to $\Delta_2 G_{\text{aq}}^\circ = \Delta_1 G_{\text{aq}}^\circ - 9.96$. We used this relation to convert the $\Delta_1 G_{\text{aq}}^\circ$ values reported for the noble gases in ref. 29 to $\Delta_2 G_{\text{aq}}^\circ$. (b) van der Waals radii are from: Mantina, M.; Chamberlin, A. C.; Valero, R.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. A* **2009**, *113*, 5806.
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