

Estimation of Bond Dissociation Gibbs Energies for Carbon–Halogen Bonds in Anion Radicals of Some Aryl Halides and Substituted Benzyl Halides

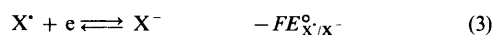
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A thermochemical cycle incorporating the standard potential $E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ}$ of aryl halides and *m*- and *p*-substituted benzyl halides RX, the standard potential $E_{\text{X}^{\cdot}/\text{X}^-}^{\circ}$ of the halide ion X^- and the bond dissociation Gibbs energy $\Delta G_{\text{BDE}}^{\circ}(\text{RX})$ of RX is used to determine the bond dissociation Gibbs energy $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ of the carbon–halogen bond in some anion radicals $\text{RX}^{\cdot-}$. The values of $E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ}$ are not directly measurable for most benzylic substrates but can be approximated by the standard potentials for the corresponding compounds in which the CH_2X group is replaced by an H atom. The calculations are compared with experimental results and similar calculations published recently.

The determination of thermodynamic parameters using thermochemical cycles has been a subject of increasing interest in recent years. By this procedure inaccessible parameters such as standard potentials, dissociation constants for weak acids and bond dissociation energies, most commonly for C–H bonds in anion radicals, cation radicals and neutral molecules, have been estimated.¹ In this paper we report on the determination of bond dissociation Gibbs energies for the carbon–halogen (C–X) bond in anion radicals of substituted benzyl halides and aryl halides RX. Recently a similar investigation has been performed for the substituted benzyl halides² but the results reported therein are not in agreement with those presented here.

The thermochemical cycle which can be used for the determination of the C–X bond dissociation Gibbs energies $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ for anion radicals in solution is shown in Scheme 1.



Scheme 1

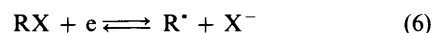
Reaction (4) is one of the key steps in the $\text{S}_{\text{RN}}1$ mechanism³ and $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ is therefore of interest in order to predict the feasibility of this reaction. According to the thermochemical cycle, $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ can be expressed as shown in eqn. (5) by

$$\begin{aligned} \Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-}) &= \Delta G_{\text{BDE}}^{\circ}(\text{RX}) + F(E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ} - E_{\text{X}^{\cdot}/\text{X}^-}^{\circ}) \approx \\ &\Delta H_{\text{BDE}}^{\circ}(\text{RX}) - T[S_f^{\circ}(\text{X}^{\cdot})_g + \Delta S_{\text{sol}}^{\circ}(\text{X}^{\cdot})] + \\ &F(E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ} - E_{\text{X}^{\cdot}/\text{X}^-}^{\circ}) \quad (5) \end{aligned}$$

the bond dissociation Gibbs energy $\Delta G_{\text{BDE}}^{\circ}(\text{RX})$ of the C–X bond in RX and the standard potentials $E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ}$ and $E_{\text{X}^{\cdot}/\text{X}^-}^{\circ}$ for the two electrode processes (1) and (3). The Gibbs energy $\Delta G_{\text{BDE}}^{\circ}(\text{RX})$ in solution can be derived from the corresponding enthalpy, $\Delta H_{\text{BDE}}^{\circ}(\text{RX})$, the entropy of formation of the halogen atom X^{\cdot} in the gas phase, $S_f^{\circ}(\text{X}^{\cdot})_g$, and the entropy of solvation of X^{\cdot} , $\Delta S_{\text{sol}}^{\circ}(\text{X}^{\cdot})$. In the derivation of eqn. (5) the common assumption that the entropy terms of RX and R^{\cdot} are expected to be nearly equal has been applied.⁴ The entropy of solvation for the halogen atoms is not known but Parker⁵ has estimated it to be in the order of $-63 \text{ J mol}^{-1} \text{ K}^{-1}$. The terms $\Delta H_{\text{BDE}}^{\circ}(\text{RX})$ † and $S_f^{\circ}(\text{X}^{\cdot})_g$ are known in the literature for the compounds

investigated in this report and they are summarized in Table 1.^{7,8}

The standard potentials $E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ}$ and $E_{\text{X}^{\cdot}/\text{X}^-}^{\circ}$ are, in most cases, not directly measurable by conventional methods such as electrochemistry or pulse radiolysis. However, for the $\text{X}^{\cdot}/\text{X}^-$ couple the potentials have been calculated from a thermochemical cycle in aqueous solution⁹ and they can easily be referred to a number of solvents by applying the known values of Gibbs energy for transferring ions X^- from water to the solvent of interest.¹⁰ The Gibbs energy of transfer for X^{\cdot} is assumed to be negligible.⁹ The potentials $E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ}$ on the other hand are not easily achievable. The values used in the paper published recently² were determined electrochemically from the direct reduction of RX. Unfortunately this procedure does not take into account that the determination is hampered seriously if the electron transfer is concerted with the bond breaking process [eqn. (6)], which is the case for most benzyl



halides.¹¹ In such a dissociative electron transfer process the electron is injected directly into the σ^* orbital of the C–X bond and the reduction potential is better described by $E_{\text{RX}/\text{R}^{\cdot} + \text{X}^-}^{\circ}$ which has a considerably more positive value than $E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ}$. For many alkyl systems the determination is also affected by the fact that the potentials are determined from waves influenced by slow heterogeneous kinetics which will shift the waves towards more negative potentials. If this shift is appreciable, the experimentally determined potentials might in principle get close to the values of $E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ}$. However, for the conjugated benzyl systems such a shift is far too small to counterbalance the large shift due to the concerted electron transfer–bond breaking process.

For aryl halides and nitrosubstituted benzyl halides the bond breaking is not concerted with the electron transfer. The anion radical $\text{RX}^{\cdot-}$ has a certain life time and the standard potential $E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ}$ can be measured directly by fast cyclic voltammetry or redox catalysis.^{11,12} For instance the standard potentials of *m*- and *p*-nitrobenzyl chloride have been found to be equal to -0.80 and -0.90 V vs. NHE in *N,N*-dimethylformamide (DMF), respectively. In these cases the electron is initially added into the π^* orbital followed by an intramolecular electron transfer to the σ^* orbital of the C–X bond. The standard potentials are thus related to the energy level of the π^* orbital in the compounds and are expected to be very close

† The values of $\Delta H_{\text{BDE}}^{\circ}(\text{RX})$ originate from determinations both in solution and gas phase. The agreement between the two sets is normally excellent.⁶

Table 1 Bond dissociation Gibbs energies $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ for variously substituted benzyl halides and aryl halides in DMF at 298 K. Included are also $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ values for the C-NO₂ bond in nitrobenzene and the C-CN bond in benzonitrile.

| Substrate | $\Delta H_{\text{BDE}}^{\circ}(\text{RX})^a$ | $S_{\text{f}}^{\circ}(\text{X}^{\cdot})^d$ | $E_{\text{RX/RX}^{\cdot-}}^{\circ e}$ | $E_{\text{X}^{\cdot}/\text{X}}^{\circ i}$ | $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})^k$ | |
|--|--|--|---------------------------------------|---|---|------------------|
| | | | | | this work | lit. |
| C ₆ H ₅ CH ₂ Br | 249 | 175.0 | -3.20 ^f | 1.5 | (-238) | 10 ^m |
| <i>p</i> -FC ₆ H ₄ CH ₂ Br | 246 | 175.0 | -2.73 | 1.5 | (-196) | 10 ^m |
| <i>m</i> -FC ₆ H ₄ CH ₂ Br | 239 ^b | 175.0 | -2.73 | 1.5 | (-203) | |
| <i>p</i> -ClC ₆ H ₄ CH ₂ Br | 241 ^b | 175.0 | -2.54 | 1.5 | (-182) | |
| <i>m</i> -ClC ₆ H ₄ CH ₂ Br | 238 ^b | 175.0 | -2.54 | 1.5 | (-185) | |
| <i>p</i> -BrC ₆ H ₄ CH ₂ Br | 241 | 175.0 | -2.20 | 1.5 | (-149) | 14 ^m |
| <i>m</i> -BrC ₆ H ₄ CH ₂ Br | 237 ^b | 175.0 | -2.20 | 1.5 | (-153) | 11 ^m |
| <i>p</i> -CNC ₆ H ₄ CH ₂ Br | 228 | 175.0 | -2.00 ^g | 1.5 | -143 | 13 ^m |
| <i>m</i> -CNC ₆ H ₄ CH ₂ Br | 234 ^b | 175.0 | -2.00 ^g | 1.5 | -137 | |
| <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Br | 228 ^b | 175.0 | -0.84 | 1.5 | -31 | 73 ^m |
| <i>m</i> -NO ₂ C ₆ H ₄ CH ₂ Br | 230 ^b | 175.0 | -0.84 | 1.5 | -29 | 49 ^m |
| C ₆ H ₅ CH ₂ Cl | 302 | 165.2 | -3.20 ^f | 1.8 | (-211) | -27 ^m |
| <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Cl | 278 ^c | 165.2 | -0.90 ^h | 1.8 | -13 | |
| <i>m</i> -NO ₂ C ₆ H ₄ CH ₂ Cl | 278 ^c | 165.2 | -0.80 ^h | 1.8 | -3 | |
| C ₆ H ₅ CH ₂ I | 202 | 180.8 | -3.20 ^f | 1.0 | (-238) | |
| C ₆ H ₅ F | 526 | 158.8 | -2.73 | 2.9 | -46 | -42 ⁿ |
| C ₆ H ₅ Cl | 400 | 165.2 | -2.54 | 1.8 | -49 | -75 ⁿ |
| C ₆ H ₅ Br | 337 | 175.0 | -2.20 | 1.5 | -53 | -71 ⁿ |
| C ₆ H ₅ NO ₂ | 298 | 240.1 | -0.84 | 0.7 ^j | 97 ^l | |
| C ₆ H ₅ CN | 548 | 202.6 | -2.00 ^g | 2.1 | 111 ^l | |

^a In kJ mol⁻¹, ref. 7. ^b Estimated from the Hammett equation given in ref. 7 (a) and the σ_m and σ_p values given in ref. 13. ^c Estimated under the assumption that the influence of the nitro group on the strength of the C-Cl bond is the same as on the C-Br bond. ^d In J mol⁻¹ K⁻¹, ref. 8. ^e In V vs. NHE, ref. 14 unless otherwise indicated. For most of the benzylic compounds the $E_{\text{RX/RX}^{\cdot-}}^{\circ}$ values are approximated by standard potentials for the corresponding arenes in which the CH₂X group is replaced by an H atom. ^f Measured in 1,2-dimethoxyethane at -60 °C. ^g From ref. 12 (a). ^h From ref. 11. ⁱ In V vs. NHE, ref. 9 and 10. ^j The Gibbs energy of transfer for NO₂⁻ from water to DMF is set equal to the corresponding energy for SCN⁻. ^k In kJ mol⁻¹. ^l The entropy of solvation for the cyano and nitro radical is assumed to be the same as for the halogen atoms. ^m In acetonitrile, ref. 2. ⁿ In acetonitrile, ref. 5.

to the standard potential of nitrobenzene, since the electronic effect of the CH₂X group is rather neutral and therefore similar to a hydrogen atom.¹³ Experimentally this is also found to be the case; the standard potential of nitrobenzene is equal to -0.84 V vs. NHE in DMF.¹⁴ From the similarity between E° for nitrobenzene and nitrosubstituted benzyl chloride and considering the experimental difficulties in estimating $E_{\text{RX/RX}^{\cdot-}}^{\circ}$ directly for the other benzylic compounds, it seems reasonable to anticipate that $E_{\text{RX/RX}^{\cdot-}}^{\circ}$ can be approximated by the standard potentials for the corresponding arenes in which the CH₂X group is replaced by an H atom. The latter potentials are measurable by electrochemical means.

The values of $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ thus calculated are shown in column 6 in Table 1 together with results collected from the literature (column 7). The calculations were performed using DMF as solvent since most of the available data was obtained in this solvent. However, $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ is expected to be of similar size in other aprotic solvents such as acetonitrile, dimethyl sulfoxide and 1-methyl-2-pyrrolidinone. The uncertainty is, in general, estimated to be ± 20 kJ mol⁻¹ the exceptions being the values given in parenthesis, where the uncertainty is larger due to the approximation in the determination of $E_{\text{RX/RX}^{\cdot-}}^{\circ}$. In the latter cases AM1 calculations* of the orbitals in the anion radicals RX^{·-} show that the electron density in the SOMO is not only located in the π -electron system as it is for nitrobenzyl chloride anion radical, but also in the σ -bond between the carbon and halogen atom. A comparison of the calculated energy difference between RX and RX^{·-} with the difference between the corresponding arene

compounds suggests that the potentials $E_{\text{RX/RX}^{\cdot-}}^{\circ}$ might be underestimated by 0.2–0.5 V (i.e. the real value of $E_{\text{RX/RX}^{\cdot-}}^{\circ}$ is more positive). The values of $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ given in parenthesis should therefore be considered to be a minimum value with a more realistic one being ca. 20–50 kJ mol⁻¹ higher.

For most of the benzylic compounds the values of $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ given in column 6 in Table 1 are very negative, which indicates that the position of the equilibrium (4) for practical purposes is completely shifted to the right. This is in accordance with the dissociative character of an electron transfer to these kinds of substrates. The bond dissociation Gibbs energy increases as expected as a function of the electron-withdrawing ability of the substituent positioned on the benzene ring. Furthermore $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ seems to be rather independent of the halogen X in contrast to the case for the parent compound RX.

For the anion radicals of aryl halides and nitrosubstituted benzyl halides, which are known to have a certain life time before splitting to halide and a carbon-centred radical, the $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ values are as expected less negative. The rate constants for the bond breaking process in the anion radicals of *m*-nitrobenzyl chloride and *p*-nitrobenzyl chloride have been measured to 80 and 4×10^6 s⁻¹, respectively.¹¹ In the anion radicals of *p*-nitrobenzyl bromide¹¹ and aryl halides¹² the bond breaking is known to occur faster in agreement with the trend in the $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ values.

Included in Table 1 are also results for the strength of the C-NO₂ and C-CN bonds in the anion radicals of nitrobenzene and benzonitrile. From the positive values of $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ the reverse step of (4) would be expected to be rather favourable in these two cases. This prediction is in accordance with experimental knowledge. The reaction between nitrite ion and phenyl radical is known to be a fast reaction forming the stable nitrobenzene anion radical as proved by EPR spectroscopy.¹⁵ Also the reaction between phenyl radical and cyanide ion has

* The AM1 calculations were performed on a Macintosh Quadra 700 using the program package MOPAC written by James J. P. Stewart. Prof. K. A. Jørgensen is thanked for providing the facilities for the theoretical calculations.

been shown to proceed quickly in ammonia at $-40\text{ }^{\circ}\text{C}$ by means of electrochemical measurements.¹⁶ The anion radical of benzonitrile is not completely stable in DMF decaying slowly to CN^- and benzene but the mechanism does not involve splitting of the anion radical as for the aryl halides. The rate determining step is reported to be an initial proton transfer step.¹⁷

In column 7 in Table 1 bond dissociation Gibbs energies collected from other sources in the literature are presented.^{2,5} In general, the values of $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ for the aryl halides are in accordance with the literature values whereas they differ appreciably for the benzyl halides. The origin of the latter rather big discrepancy can be mainly attributed to the use of irreversible reduction potentials in ref. 2 instead of $E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ}$. The mistake thereby made is considerable and in the order of 1–2 V in terms of potentials or of 96–193 kJ mol^{-1} in terms of bond dissociation Gibbs energies. The literature values also suffer from an inconsistency in the reference electrode used for the determination of the potentials $E_{\text{X}^{\cdot-}/\text{X}^-}^{\circ}$ and $E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ}$. While $E_{\text{X}^{\cdot-}/\text{X}^-}^{\circ}$ is referred to the standard hydrogen electrode in the actual solvent used (acetonitrile),¹⁴ $E_{\text{RX}/\text{RX}^{\cdot-}}^{\circ}$ is referred to the normal hydrogen electrode (in aqueous medium by definition). This results in an additional consistent error in $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ of 46 kJ mol^{-1} corresponding to the Gibbs energy of transfer for the proton between the two solvents. Finally, the entropy terms of the halogen atom X^{\cdot} are not incorporated in the calculations in ref. 2 leading to a further difference of about 30 kJ mol^{-1} . The results presented here are therefore believed to be more accurate than those reported previously.

Summary.—Calculations of bond dissociation Gibbs energies $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ of anion radicals using a thermochemical cycle can be used for predicting the feasibility of a reaction mechanism such as $\text{S}_{\text{RN}}1$. However, in the calculations careful attention to the thermodynamic significance of the parameters involved in the cycle has to be taken. The use of irreversible potentials and mixing of enthalpy and Gibbs energy terms² should be avoided since errors in the order of 200 kJ mol^{-1} may be introduced. For the substrates investigated here the values of $\Delta G_{\text{BDE}}^{\circ}(\text{RX}^{\cdot-})$ show that the $\text{S}_{\text{RN}}1$ step involving the coupling between an anion and a radical is favourable only for the phenyl radical and nitrite or cyanide ion. In the other cases

the anion radicals formed are unstable and will immediately split into the radical and anion. This is particularly the case for unsubstituted benzyl halides while the anion radicals of nitro-substituted benzyl halides should possess a certain stability. These predictions are in agreement with experimental results.

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