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Using inherent radical stabilization energies to predict unknown enthalpies of formation and associated bond dissociation energies of complex molecules

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ABSTRACT

Many free radical reactions are used currently for syntheses not easily accomplished by other methods. Hence, there is an increasing need for information about bond dissociation energies and enthalpies of formation of the molecules and radicals than is currently available for the more complex species involved in such reactions. We provide 98 standard enthalpies of formation that are not available in the extensive NIST database (number 69), 127 bond dissociation energies not experimentally available, and many previously unknown or uncertain enthalpies of formation of radicals, all at 298 K. A method is presented that allows one to obtain good predictions of the thermodynamic properties of new species using the inherent radical stabilities of their components. The information should be useful for designing and rationalizing synthetic radical reactions.

1. Introduction

Free radicals play a vital role in many enzyme reactions, polymerizations, the ageing process, combustion, and increasingly in syntheses that cannot be easily accomplished by non-radical reactions. As more and more radical reactions are used in syntheses, more complex molecules are involved with various functionalities and thermodynamic quantities that are not very well known either for the molecules themselves or for the radicals involved. Generally, gas phase standard enthalpies of formation, $\Delta_f H^\circ$, are known more accurately for closed shell species than they are for free radicals.

There are many experimentally obtained or theoretically calculated enthalpies of formation of radicals, $\Delta_f H^\circ[R\bullet]$ gas phase at 298 K, available in the literature. However by themselves, $\Delta_f H^\circ[R\bullet]$ values cannot establish bond dissociation energies of molecules formed by their combination. If the enthalpy of formation of a molecule R–R′ is available, then values of $\Delta_f H^\circ[R\bullet]$ and $\Delta_f H^\circ[\bullet R']$ can be used to obtain bond dissociation energies of D[R–R′] of various reactants and products and establish whether a radical reaction will be endothermic or exothermic and by how much. This would be of help in designing synthetic reactions. The problem is that, for many relatively complex RR′ molecules involved in current synthetic work, enthalpies of formation $\Delta_f H^\circ[RR']$ are not available. The present work addresses this issue. We report enthalpies of formation of 98 compounds for which the extensive NIST database number 69 does not provide experimental gas phase values.[1] We also provide 127 previously unavailable bond dissociation energies and enthalpies of formation of 91 radicals many of which were previously unavailable experimentally, or either have large stated uncertainties, or available values which are in significant disagreement. We then use these values to demonstrate a method for estimating heats of formation at 298 K for new compounds based on the inherent radical stabilization energies of their components.

We have previously reported over 800 bond dissociation energies for species forming carbon- and heteroatom-centered radicals, R•, by homolytic bond cleavage of R–H, R–CH_3, R–Cl, and R–R molecules, all gas phase values at 298 K.[2,3] The energies were obtained by calculations at the G3(MP2)-RAD//B3-LYP/6-31G(d) level of theory, a high level composite ab initio molecular orbital theory,[4] and the details have been described.[2,3] This method has been shown to reproduce a large set of gas phase experimental data to within 'chemical accuracy' and showed similar accuracy for known bond dissociation energies and radical stabilities.[5] For a subset of bond dissociation energies, for which experimental values are available, the mean absolute deviation of the theoretical results from experiment is 1.8 kcal mol^{-1}. This is comparable to 1.6 kcal mol^{-1} for the various experimental values reported for the same bond.[3]

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Our previous works have established values of Pauling-type electronegativities, χ, for a large variety of R• groups and values of their radical stabilization energies, RSE, both of which were demonstrated to be inherent to the radical and transferable to different molecules.[2,3] The RSE value of a radical, R•, is defined in terms of bond dissociation energies, D, by: RSE[R•]=½(D[H_3C–CH_3]$_{calcd}$–D[R–R]$_{calcd}$). In the past, radical stabilization energies were usually defined in terms of the difference: RSE_H=D[H–CH_3]–D[H–R]. However, such values are applicable only to carbon-centered radicals. Our RSE values have the significant advantage of being applicable not only to carbon-centered radicals, but also to all heteroatom-centered ones; these values were denoted by RSE_Z in Ref. 2 and as RSE_{Et} in Ref. 3. This RSE definition cannot be used when the R–R bond is subject to 'special effects,' such as conjugation stabilization of 1,3-butadiene when R–R is CH_2=CH–CH=CH_2, or steric strain in bi-*tert*-butyl when R–R is $(CH_3)_3C$–$C(CH_3)_3$. In such cases the effect is not inherent in the radicals but arises in the molecule, and an alternative method was used, as has been described for obtaining RSE values.[2,3] The very large variety of χ and RSE values already established allows for the calculation of bond dissociation energies for a large number of bonds. The bond dissociation energy of R–R′ is obtained kcal mol^{-1} by:

$$D[R{-}R']_{calcd} = D[H_3C{-}CH_3]_{calcd} - RSE[R\bullet] - RSE[\bullet R'] + 23(\chi[R\bullet] - \chi[\bullet R'])^2 \quad (1)$$

D[R–R′]$_{calcd}$ values obtained by equation (1) have been compared to available literature values, both experimental and theoretical.[3] In all, 234 different D[R–R′]$_{calcd}$ values were compared to available bond dissociation energies and the mean absolute deviation from the literature values was 1.6 kcal mol^{-1}. In the present work, equation (1) is used to calculate bond dissociation energies for which experimentally based values do not appear to be available. Equation (1) is essentially Pauling's electronegativity relation. Although maligned in the past, Pauling's relation has been shown to produce accurate results for a very large number of known bond dissociation energies.[3,6] It fails only when misused.[6]

In the present work, gas phase standard enthalpies of formation of radicals at 298 K are obtained by equations (2) and (3), where D[R–H]$_{calcd}$ and D[R–CH_3]$_{calcd}$ are our theoretically calculated bond dissociation energies of R–H and of R–CH_3, Δ_fH°[H•]$_{lit}$ and Δ_fH°[•CH_3]$_{lit}$ are established experimental standard enthalpies of formation of H• and •CH_3 (52.1 and 34.8 kcal mol^{-1}, respectively), and Δ_fH°[RH]$_{lit}$ and Δ_fH°[RCH_3]$_{lit}$ are experimentally known gas phase standard enthalpies of formation from the literature, mostly obtained from the NIST database no. 69.[1]

$$\Delta_fH^\circ[R\bullet]_{calcd} = D[R{-}H]_{calcd} - \Delta_fH^\circ[H\bullet]_{lit} + \Delta_fH^\circ[RH]_{lit} \quad (2)$$

$$\Delta_fH^\circ[R\bullet]_{calcd} = D[R{-}CH_3]_{calcd} - \Delta_fH^\circ[\bullet CH_3]_{lit} + \Delta_fH^\circ[RCH_3]_{lit} \quad (3)$$

The same type of equations can be used with our values of D[R–Cl]$_{calcd}$ and of D[R–R]$_{calcd}$, but experimental literature values of Δ_fH°[RCl] and Δ_fH°[RR] often are not available for complex molecules. Ideally, the Δ_fH°[R•]$_{calcd}$ values obtained via equations (2) and (3) would be the same. In practice, the two values are not exactly identical, because the experimental enthalpies of Δ_fH°[RH]$_{lit}$ and of Δ_fH°[RCH_3]$_{lit}$ used in the two equations have the usual experimental uncertainties added to the uncertainties of the theoretical calculations.

Once bond dissociation energies D[R–R′]$_{calcd}$ are obtained by equation (1) and enthalpies of formation of radicals Δ_fH°[R•]$_{calcd}$ and Δ_fH°[•R′]$_{calcd}$ by equations (2) and (3), hitherto unknown enthalpies of formation are obtained by equation (4). Radical enthalpies of formation used with equation (4) are the average of the two values obtained for each by equations (2) and (3).

$$\Delta_fH^\circ[RR']_{calcd} = \Delta_fH^\circ[R\bullet]_{calcd} + \Delta_fH^\circ[\bullet R']_{calcd} - D[R{-}R']_{calcd} \quad (4)$$

2. Results

Table 1 lists the results obtained by equations (2) and (3) for 91 radicals R• for which experimental enthalpies of formation of RH and of RCH_3 are available, generally obtained from the NIST database number 69,[1] unless specified otherwise. The first group of entries contains values that are accurately known for simple radicals, with several experimental determinations giving essentially the same value. Comparison of these experimental results with those calculated by equations (2) and (3) should establish the level of accuracy to be expected for our calculated values. Differences between our two calculated values of each Δ_fH°[R•] are generally small and in only two of the radicals treated in Table 1 the difference is as high as 2.1 kcal mol^{-1}. This demonstrates the consistency and robustness of the method employed.

The second group of entries in Table 1 contains more complex radicals, including many for which literature values are in significant disagreement or have large uncertainties specified for them. Our calculated values allow a better choice to be made among previously published values or help to narrow the spread of large stated uncertainties. On a few occasions, available experimental literature values are noted to be in significant disagreement with those obtained by use of equations (2) and (3).

The third group of entries in Table 1 consists of radicals for which experimental enthalpies of formation were not found in the literature or for which only a single literature value was found.

Our recommended value for each Δ_fH°[R•] is the average of the two Δ_fH°[•R]$_{calcd}$ values obtained by equations (2) and (3), as listed in Table 1. In some cases where experimental values of Δ_fH°[RCl]$_{lit}$ and Δ_fH°[RR]$_{lit}$ are available, Δ_fH°[R•] values calculated via our theoretical D[R–Cl] and D[R–R] are in agreement with those of Table 1. For example, Δ_fH°[•CH_2CH_3] is 28.1 via D[CH_3CH_2–Cl]$_{lit}$ and 28.9 via D[CH_3CH_2–CH_2CH_3]$_{lit}$, essentially the same as 28.7 and 28.4 listed in Table 1 via D[CH_3CH_2–H]$_{lit}$ and via D[CH_3CH_2–CH_3]$_{lit}$, respectively. For the 2-methyl-1-propyl radical (isobutyl), equations (2) and (3) produce Δ_fH°[R•]=18.0 and 16.0 kcal mol^{-1}, respectively, as an example of significant disagreement. When obtained via the theoretically calculated D[Cl–$CH_2CH(CH_3)_2$ of 85.4 kcal mol^{-1},[2] the result is Δ_fH°[R•]=17.7, straddling the other two values and near their average of 17.5. This type of agreement further confirms the consistency of the method in using equations (2) and (3).

Table 2 uses equation (1) to obtain bond dissociation energies of R–R′ molecules using radical stabilization energies, RSE, and electronegativity values, χ, reported in our previous works.[2,3] The value used for D[H_3C–CH_3]$_{calcd}$ is the one theoretically obtained, 88.6 kcal mol^{-1}, for consistency with all our other theoretical values. The RSE and χ values of R and R′ are shown in the Table along with the bond dissociation energies obtained. The values of the calculated enthalpies of formation of radicals R• and •R′ reported in Table 1 are then used with equation (4) to obtain standard enthalpies of formation of RR′. The RR′ molecules chosen for this work are primarily those for which no gas phase values are listed the NIST database.[1]