Comment on "Radicalicity: A Scale to Compare Reactivities of Radicals"

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Abstract

The recently proposed term “radicalicity” was described as a measure of the reactivity of a free radical Q•, i.e., a kinetic quantity. It is shown here that in fact it is simply a frame-shifted version of the well-known bond dissociation energy, a thermodynamic quantity. Hence its use is discouraged.

The history of mechanistic free-radical chemistry contains numerous examples of a failure to distinguish between the *stability* of a radical, which is a thermodynamic property characterized by its heat of formation $\Delta_f H^o$, and its *persistence* or *reactivity*, which is a kinetic quantity characterized by a rate constant or Arrhenius parameters for a defined reaction [1]. An example of this confusion is embedded in a recent publication by Fiser and workers [2] who define a new scale which they claim to "compare quantitatively the reactivity of different radical species" whereas, as we show below, it contains only thermodynamic rather than kinetic information.

To formulate the new scale of "radicalicity" said to characterize the *reactivity* of a wide range of free radicals Q•, the test reaction was hydrogen atom transfer from molecular hydrogen (eqn 1). The thermodynamics, i.e., the

$$Q\bullet + H\text{–}H \rightarrow QH + H\bullet \qquad (1)$$

standard-state enthalpies $\Delta_r H$ and free energies $\Delta_r G$ of reaction, were obtained by computations at the G3MP2B3 level for the structures, energy levels, and vibrational frequencies of the ground states QH and Q•. These were then expressed relative to the corresponding parameters for Q• = HOO• as a reference point (eqn 2; $Y = H$ or G) and a dimensionless ratio was defined by eqn 3 based on the most "reactive" radical OH• and verbalized by the term "radicalicity", R(%). We express R(%) by the expanded form in eqn 4. This form emphasizes that the quantities involved in the definition of R(%) are in fact all heats of formation or free energies of formation. Finally then, for $Y = H$, we have eqn 5 where BDE is the familiar bond dissociation energy [3]: BDE(Q—H) = $\Delta_f H^o$(Q•) – $\Delta_f H^o$(QH) + $\Delta_f H^o$(H•). This form reveals that R(%) is simply a frame-shifted version of the thermochemical quantity BDE(Q−H) and contains no kinetic information regarding eqn 1.

$$\Delta_{\mathrm{rel}}Y^{\mathrm{o}}(\mathrm{Q}\bullet) = \Delta_{\mathrm{r}}Y^{\mathrm{o}}(\mathrm{Q}\bullet) - \Delta_{\mathrm{r}}Y^{o}(\mathrm{HOO}\bullet) \qquad (2)$$

$$R(\%) = 100\ [\Delta_{\mathrm{rel}}Y^{\mathrm{o}}(\mathrm{Q}\bullet)]\ /\ [\Delta_{\mathrm{rel}}Y^{\mathrm{o}}(\mathrm{OH}\bullet)] \qquad (3)$$

$$\begin{aligned} R(\%) = 100\ [&\Delta_{\mathrm{f}}Y^{\mathrm{o}}(\mathrm{Q}\bullet) - \Delta_{\mathrm{f}}Y^{\mathrm{o}}(\mathrm{QH}) - \Delta_{\mathrm{f}}Y^{\mathrm{o}}(\mathrm{HOO}\bullet) + \Delta_{\mathrm{f}}Y^{\mathrm{o}}(\mathrm{HOOH})]\ / \\ [&\Delta_{\mathrm{f}}Y^{\mathrm{o}}(\mathrm{OH}\bullet) - \Delta_{\mathrm{f}}Y^{\mathrm{o}}(\mathrm{HOH}) - \Delta_{\mathrm{f}}Y^{\mathrm{o}}(\mathrm{HOO}\bullet) + \Delta_{\mathrm{f}}Y^{\mathrm{o}}(\mathrm{HOOH})] \qquad (4) \end{aligned}$$

$$\begin{aligned} R(\%) &= 100\ [\mathrm{BDE(Q–H)} - \mathrm{BDE(HOO–H)}]\ / \\ &\quad [\mathrm{BDE(HO–H)} - \mathrm{BDE(HOO–H)}] = \\ &\quad 100\ [\mathrm{BDE(Q–H)} - 365.7)]\ /\ [497.3 - 365.7] = \\ &\quad 0.76\ \mathrm{BDE(Q–H)\ (kJ/mol)} - 278 \qquad (5) \end{aligned}$$

As already noted, the goal of the study [2] was explicitly stated to be to “compare quantitatively the reactivity of different radical species” and it was concluded that “$\Delta_{\mathrm{rel}}G^{\mathrm{o}}$ is a measure of the relative reactivity of the radical, so OH has the highest reactivity. . .while NO has the weakest reactivity among the species considered. . .” Yet we note that nowhere are computations of transition states for eqn 1 or its rate constants addressed, i.e., the proper measure of “reactivity”, but only measures of thermochemistry. While it is indeed true that the activation energy of a radical reaction typically decreases as its exothermicity increases, as expressed historically in the Evans-Polanyi relationship [4], it has also been recognized for over half a century that the relationship is usually not strictly linear because the rate constants are also often dependent on polar effects and steric effects [5-7] as well as thermochemical effects. Our recent studies [8-10] of the hydrogen transfer reaction by Cl•, OH•, and Br• and references therein will suffice to illustrate this fact.

Therefore we suggest that the term “radicalicity”, presented [2] as a measure of radical *reactivity*, not be adopted because it is in reality simply another expression for *thermochemistry* for which there is already adequate terminology (BDE).

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