On the O–H bond dissociation enthalpy of catechol

Opinion

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There are different estimations on the relative O–H bond dissociation enthalpy (BDE) of catechol, ranging from 4.6 kcal mol^{-1} to 14.1 kcal mol^{-1} lower than that of phenol. Through a kinetic analysis, the relative O–H BDE of −7.2 kcal mol^{-1} was supported.

The O–H bond dissociation enthalpy (BDE) is not only a basic physicochemical parameter, but also an important theoretical descriptor to characterize the radical-scavenging activity of phenolic antioxidants.[1] Hence, various methods, including experimental determinations[2–4] and theoretical calculations,[5] have been employed to estimate the O–H BDE. Although the two types of methods give consistent values for monophenols, the O–H BDE of catechol has given rise to much controversy.

The O–H BDE for catechol was estimated to be 9.2–14.1 kcal mol^{-1} lower than that of phenol by means of density functional theory (DFT) calculations on various basis sets.[6] The low O–H BDE for catechol was attributed to two kinds of substituent effects, the electronic effect and the intramolecular hydrogen bond (IHB) effect. The former effect results from the electron-donating property of the *ortho* hydroxyl group, while the latter arises from the 5–10 kcal mol^{-1} increment of the IHB enthalpy (H_{IHB}) for the catecholic radical compared with that for the parent catechol.[6,7] However, employing the EPR equilibration technique, the O–H BDE of 3,5-di-*tert*-butylcatechol (DTBC) was determined to be 8.2 kcal mol^{-1} lower than that of phenol.[8] By additivity analysis, the O–H BDE for catechol was estimated to be only 4.6 kcal mol^{-1} lower than that of phenol and the H_{IHB} for the catecholic radical only 4.4 kcal mol^{-1},[8] which is inconsistent with a previous experimental result.[9] In addition, through a thermal decomposition study of substituted anisoles, Pratt and co-workers indicated that the *ortho* OH or OCH_3 group reduced the O–C BDE of anisole by 7.2 or 4.1 kcal mol^{-1}, respectively.[10] Since the substituent effect on O–C BDEs of anisoles is very similar to that on O–H BDEs of phenols,[5a,10] the O–H BDE of catechol can be reasonably estimated to be ~7.2 kcal mol^{-1} lower than that of phenol, and the IHB contribution is 3.1 (7.2–4.1) kcal mol^{-1}.

As catechol is a crucial moiety for natural antioxidants to enhance radical-scavenging activity,[11] it is very important to elucidate the discrepancy in these values and determine which O–H BDE of catechol is the most reliable.

Recently, Barclay and co-workers provided a series of rate constants for substituted phenols, including catechols, to scavenge peroxyl radical (ROO$^\bullet$) (Table 1).[12] A good correlation was found between log *k* and theoretical O–H BDEs for these phenols,[12] suggesting that the transition states of these phenols to donate one hydrogen atom were similar to one another and that the theoretical O–H BDE of catechol, 10 kcal mol^{-1} lower than that of phenol, was reliable. However, considering the fact that the theoretical O–H BDEs of the monophenols employed in their work are systematically lower than the experimental values, we think it would be better to use the experimental O–H BDEs for monophenols to extrapolate the O–H BDE of catechol.

By means of the EPR equilibration technique, Pedulli, Lucarini and co-workers have determined relative O–H BDEs for various monophenols (Table 1).[13,14] As shown in Fig. 1, there exists a good linear relationship between log *k* and the experimental relative O–H BDEs.[15] According to the regression equation, the relative O–H BDE of catechol was estimated to be −6.9 kcal mol^{-1} (Table 1), which supports the value derived from the thermal decomposition study, −7.2 kcal mol^{-1}, and is a good compromise between the theoretical results and EPR experimental values. Thus, it seems that the EPR equilibration technique overestimated the O–H BDE of catechol, while the DFT calculations underestimated the value.

We are aware that there exists other experimental methods than the EPR equilibration technique to determine O–H BDE, such as the thermodynamic cycling method[2] and the photoacoustic calorimetry method.[4] In particular, the latter method has the advantage of determining the reaction enthalpy directly. Thus, we hope the extrapolated O–H BDE of catechol will be verified by further experiments and higher-level theoretical calculations.

Last but not least, it should be pointed out that the present O–H BDE of catechol was derived from the experimental results obtained in nonpolar solvents, such as hexane and benzene,[12,13] thus the parameter is comparable to that in the gas phase and has to be used with caution in polar solvents. In the latter case, solvent effects may considerably influence the radical scavenging mechanism and IHB of catechols, which

Table 1 Logarithm of the rate constants for substituted phenols to scavenge peroxyl radical (ROO$^\bullet$) and the relative O–H bond dissociation enthalpies (BDEs) for substituted phenols

Substituted phenols	log $k_{\mathrm{ROO}^\bullet}$[a]	Relative O–H BDE[b] /kcal mol^{-1}
4-CN-Phenol	2.63	1.4
Phenol	3.63	0
3-Me-Phenol	3.65	−0.5
3-MeO-Phenol	3.57	−0.45
4-Cl-Phenol	3.50	−0.4
4-Me-Phenol	4.13	−1.7
4-MeO-Phenol	4.84	−4.4
PMHC[c]	6.52	−9.4
Catechol	5.74	−6.9[d]

[a] Data from ref. 12. [b] Data from ref. 13. [c] 2,2,5,7,8-Pentamethyl-6-hydroxychroman. [d] Extrapolated value from regression equation.

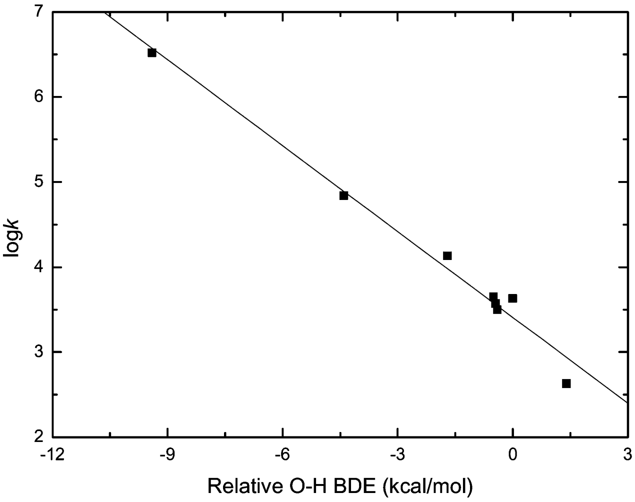

Fig. 1 Correlation between log k and experimental relative O–H BDE for monophenols. Regression equation: $Y = 3.41 - 0.34 \cdot X$, $r = -0.99$.

will make the O–H BDE invalid for characterizing the radical scavenging activity. For instance, the radical scavenging mechanism of (+)-catechin becomes an electron-concerted proton transfer rather than a one-step hydrogen atom transfer in polar solvents such as acetonitrile,[16] thus not the O–H BDE but the ionization potential is the proper theoretical parameter to consider. On the other hand, the hydrogen bond accepting solvent will strengthen the inter- and weaken the intramolecular hydrogen bond associated with catechols, and thus will substantially decrease the radical scavenging rate constants of antioxidants with a catechol moiety such as quercetin or epicatechin, *etc.*[17,18] Therefore, in polar solvents, one cannot use solely the gas phase O–H BDE to predict the antioxidant activity of catechols, and one has to take other parameters into consideration.

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14 Denisov[1a] and Borges dos Santos[1b] have provided other sets of relative O–H BDEs by summarizing experimental results obtained from different methods or by combining experimental and theoretical results. Apparently, the O–H BDEs coming from the same experiments may be more reliable. Hence, we prefer to use Pedulli, Lucarini and co-workers' results.[13].

15 Barclay *et al.* also provided a series of rate constants for phenols to scavenge 2,2-di(4-*t*-octylphenyl)-1-picrylhydrazyl radical (DOPPH$^{\bullet}$).[12] However, only four corresponding O–H BDEs are available. Hence, we prefer to use the rate constants of scavenging ROO$^{\bullet}$, which can correlate with more O–H BDEs and thus give a more reliable regression equation.

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