Reactivity indices as a measure of rate constants for protonation of radical anions and dianions

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The DFT-based reactivity indices were used to describe protonation reactions of radical anions (RA) and dianions (DA) of aromatic compounds. A correlation between the experimental rate constants for protonation and the global reactivity indices was found. The indices were expressed through the electron affinities and ionization energies computed at the B3LYP level of theory. The protonation reactions of RA and DA of aromatic compounds are correctly described by the reactivity indices calculated as the inverse of the difference between the formal formation potential of RA (or DA) and the formal reduction potential of the proton donor.

Key words: radical anion, dianion, dinitrobenzene, quantum chemical calculations, density functional theory, B3LYP functional, PCM model.

The protonation reactions of radical anions (RA) and dianions (DA) play an important role in chemical and biochemical processes:[1—3]

$$A^{\bullet -} + BH \longrightarrow AH^{\bullet} + B^{-}, \quad (1)$$

$$A^{2-} + BH \longrightarrow AH^{-} + B^{-}. \quad (2)$$

Their theoretical description is therefore topical.

The most promising approach to evaluate the rates and regioselectivities of the reactions involving RA and DA is the method of quantum chemical reactivity indices that are calculated using parameters of the electronic structure of the reactants.[3]

Interest in this type of indices has grown considerably in the last decades,[4] as their use has received reliable theoretical (DFT) support.[5] This first of all concerns such global indices as, *e.g.*, the electronegativity (χ) and the chemical potential (μ),[6] the hardness (η) and the softness (S),[7] the electrophilicity (ω),[8] and the nucleophilicity ($\bar{\omega}$),[9] as well as some local indices corresponding to a specific point, *e.g.*, the softness (s)[10] and the Fukui function (f).[11]

As a reactivity index, one can also use the interaction energy between the reactants early along the reaction coordinate, where the changes in their nuclear configurations can be ignored. Approaches to evaluate the intermolecular interaction energies within DFT formalism were proposed.[12] An alternative approach implies that initially, when the reaction proceeds with a small orbital overlap, intermolecular interactions can be described using the perturbative approach.[13] The indices thus determined correctly describe the reactivity of RA belonging to diverse classes of organic compounds.[3]

Attempts to establish correlations between the electronic structures of RA and their behavior in the protonation reaction were reported.[14—18] However, the systems under study usually included aromatic hydrocarbons, and the protonation of dianions was not considered at all.

In this work we examine the possibility of describing the reactions (1) and (2) using the global reactivity indices[19] as well as the indices characterizing the interaction energy between the reactants early along the reaction coordinate.[3]

Experimental

Quantum chemical calculations of aromatic molecules were performed within the framework of the density functional theory using the B3LYP exchange-correlation functional.[20—22] As shown earlier,[23] extension of the basis set changes the calculated electron affinity values for various donor molecules without π-bonds insignificantly (by 0.05 eV at most on going from the 6-31+G(d,p) to the 6-311++G(d,p) basis set).

However, the electron affinities of the molecules with π-bonds are highly sensitive to the presence of diffuse functions on the hydrogen atoms in the basis set and may change by up to 1.0 eV on going to the 6-311++G(d,p) basis set. Therefore, all calculations in this work were carried out with the 6-311++G(d,p) basis set.

The solvent effect was included by using the self-consistent reaction field and polarized continuum methods (PCM)[24—26]

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with the parameters for DMSO similar to those of DMF (used in the experiment). All calculations were carried out with the Gaussian-03 program package.[27]

Results and Discussion

Tables 1—3 present the rate constants (k) for protonation of RAs and DAs of nitro derivatives of benzene,[28—30] naphthalene,[3] and anthracene[3] determined by cyclic voltammetry and chronoamperometry, as well as the DFT calculated vertical and adiabatic electron affinity (EA) and ionization energy (IE) values. These data were used to derive such reactivity indices as the chemical potential (μ), the global hardness (η) and softness (S), as well as the energy change due to charge transfer from the base to a proton donor (ΔE_{ct}).

The concept of reactivity indices implies the following relation between the rate constant (k) and the reactivity index (I):

$$\log k = a + bI. \quad \text{(I)}$$

The corresponding correlation coefficients (R^2) for the dependence (I) of the rate constants for reactions (1) and (2) on various reactivity indices are as follows:

Index	R^2	Index	R^2
μ	0.530	$1/(EA_v - IE_v)$	0.895
η	0.687	$1/(EA_a - IE_a)$	0.842
S	0.854	$1/\Delta E^\circ$	0.875
ΔE_{ct}	0.837		

As can be seen, experimental rate constants for protonation are in a good correlation with S and ΔE_{ct}. These correlations were constructed using only the global indices that are non-specific to a given reaction center. The correlation coefficient can likely be improved by the use of some local indices. The latter, however, require the appropriate Fukui functions for the reaction center to be computed.[33—35] Such computations involve inclusion of explicit solvent molecules in the solvation shell and are thus very time-consuming.[36]

Earlier,[3] the reactions of RA were successfully described using the perturbation theory formalism and the frontier orbital concept (HOMO and LUMO).[37] As applied to Reaction (1), this approach allowed one to account also for the nature of not only RAs, but also proton donors. In particular, the logarithms of experimental rate constants for the protonation of alternant hydrocarbons with water, propan-2-ol, and phenol were shown[3] to correlate with the reactivity indices expressed as:

$$I = c_s^2/|\varepsilon_m - \varepsilon_n|, \quad \text{(II)}$$

where c_s is the amplitude of the frontier MO wave function on the reaction center, and ε_m and ε_n are the HOMO and LUMO energies of the base and proton donor, respectively.

Neglecting the variations of c_s^2 over the reaction series allows one to use a simpler index:

$$I_1 = 1/|\varepsilon_m - \varepsilon_n|.$$

In the context of Koopmans´ theorem, ε_m and ε_n can be replaced by the vertical ionization energy (IE_v) of the base and the vertical electron affinity (EA_v) of the proton donor. This gives the best correlation between theory

Table 1. Vertical (EA_v) and adiabatic (EA_a) electron affinities of substrate molecules

Molecule*	EA_v	EA_a
	eV	
NB	3.17	3.59
1,2-DNB	3.60	4.06
1,3-DNB	3.53	3.87
1,4-DNB	3.87	4.21
Naphthalene	1.58	1.88
Anthracene	2.21	2.44
Phenol	0.77	1.18

* Hereafter, NB and DNB denote nitrobenzene and dinitrobenzene, respectively.

Table 2. Vertical (EA_v) and adiabatic (EA_a) electron affinities, vertical (IE_v) and adiabatic (IE_a) ionization energies, and the logarithms of the rate constants for protonation of RAs of substrate molecules

Molecule	EA_v	EA_a	IE_v	IE_a	log$k$
	eV				
NB	1.89	2.23	3.84	3.59	1.57[28]
1,2-DNB	2.93	3.31	4.34	4.06	2.0[31]
1,3-DNB	3.08	3.50	4.10	3.87	<–2.3[32]
1,4-DNB	3.14	3.41	4.48	4.21	<–2.3[32]
Naphthalene	1.58	0.96	1.84	1.88	5.1[3]
Anthracene	1.39	1.58	2.41	2.44	3.4[3]

Table 3. Vertical (IE_v) and adiabatic (IE_a) ionization energies and the logarithms of the protonation rate constants for DAs of substrate molecules

Molecule	IE_v	IE_a	log$k$
	eV		
NB	2.44	2.23	—
1,2-DNB	3.68	4.06	2.4[31]
1,3-DNB	3.70	3.87	2.0[32]
1,4-DNB	3.67	4.21	1.1[32]
Naphthalene	0.85	1.88	—
Anthracene	1.56	1.58	—

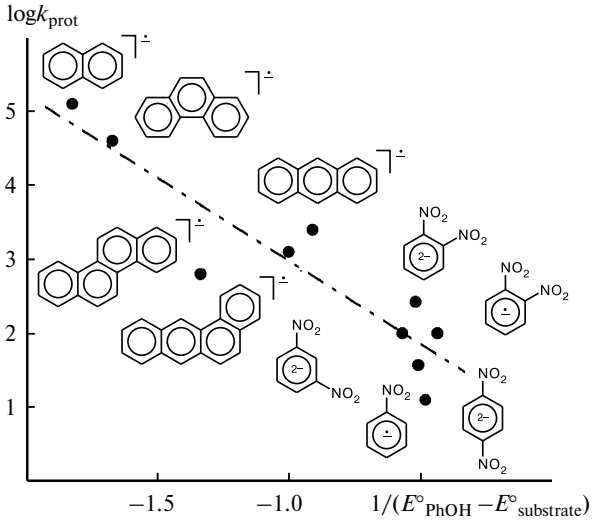

Fig. 1. Rate constants for protonation of RAs of naphthalene, phenanthrene, chrysene, 1,2-benzanthracene, anthracene, 1,2-DNB, nitrobenzene, and DA of 1,3-DNB, 1,2-DNB, and 1,4-DNB plotted *vs.* difference between the formal reduction potentials of proton donors and substrates (protonation with phenol in DMF).

and experiment ($R^2 = 0.895$). The more available adiabatic values do not significantly decrease the correlation coefficient ($R^2 = 0.842$). This enables estimation of the reactivity indices using the formal reduction potentials, E°, which can be determined with ease in the experiments.*

As shown earlier,[38] the energies of formation of RA and DA for the compounds under study, E°, correlate linearly with the theoretical adiabatic electron affinity values. Consequently, the use of the inverse of the difference between the formal potentials as a reactivity index increases the correlation coefficient to 0.875 (see above) rather than decreases it.

In Fig. 1, the logarithms of the rate constants for reactions (1) and (2) are plotted against the inverse of the formal potential difference for the compounds listed in Tables 1—3, as well as for RAs of phenanthrene, chrysene, and 1,2-benzanthracene.[39] As can be seen, the extension of the reaction series does not significantly decrease the correlation coefficient ($R^2 = 0.843$).

In conclusion, the rate constants for protonation of RA and DA can be estimated from experimentally determined formal potentials of formation of RA and DA as well as the formal reduction potentials of proton donors**.

* Since phenol is non-reducible in the experimentally available potential range, its E° value was determined from the theoretical electron affinity value and the correlation obtained earlier.[38]

** For proton donors that are difficult to reduce, E° can be evaluated using the correlation between their electron affinity and formal reduction potential.

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References

1. *Hydrogen-Transfer Reactions*, Eds J. T. Hynes, J. P. Klinman, H. H. Limbach, R. L. Schowen, Wiley-VCH, Weinheim, 2007.
2. *Proton-Transfer Reactions*, Eds E. Caldin, V. Gold, Chapman and Hall, London, 1975, 448 pp.
3. A. I. Rusakov, A. S. Mendkovich, V. P. Gul´tyai, V. Yu. Orlov, *Struktura i reaktsionnaya sposobnost´ organicheskikh anion-radikalov* [*Structure and Reactivity of Organic Radical Anions*], Mir, Moscow, 2005, 294 pp. (in Russian).
4. P. Geerlings, F. De Proft, W. Langenaeker, *Chem. Rev.*, 2003, **103**, 1793.
5. R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1998.
6. D. M. York, W. Yang, *J. Chem. Phys.*, 1996, **104**, 159.
7. S. Liu, F. De Proft, R. G. Parr, *J. Phys. Chem. A*, 1997, **101**, 6991.
8. P. Perez, L. R. Domingo, M. J. Aurell, R. Contreras, *Tetrahedron*, 2003, **59**, 3117.
9. J. L. Gazquez, A. Cedillo, A. Vela, *J. Phys. Chem. A*, 2007, **111**, 1966.
10. W. Yang, R. G. Parr, *Proc. Natl. Acad. Sci. USA*, 1984, **82**, 6723.
11. P. W. Ayers, F. De Proft, A. Borgoo, P. Geerlings, *J. Chem. Phys.*, 2007, **126**, 224107.
12. Y. Li, N. S. Evans, *J. Am. Chem. Soc.*, 1995, **117**, 7756.
13. M. J. S. Dewar, R. C. Dogherty, *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975.
14. R. G. Pearson, *J. Am. Chem. Soc.,* 1963, **85**, 3533.
15. P. K. Chattaraj, H. Lee, R. G. Parr, *J. Am. Chem. Soc.*, 1991, **113**, 1855.
16. H. Chermette, *J. Comput. Chem.*, 1999, **20**, 129.
17. R. G. Parr, R. G. Pearson, *J. Am. Chem. Soc.*, 1983, **105**, 7512.
18. K. R. S. Chandrakumar, S. Pal, *Int. J. Mol. Sci.*, 2002, **3**, 324.
19. Yu. Z. Zevatskii, D. V. Samoilov, *Zh. Organ. Khimii*, 2007, **43**, 487 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2007, **43**].
20. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
21. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
22. S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.
23. M. N. Mikhailov, N. D. Chuvylkin, I. V. Mishin, L. M. Kustov, *Zh. Fiz. Khimii*, 2009, **83**, 868 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 2009, **83**].
24. J. Tomassi, M. Persico, *Chem. Rev.*, 1994, **94**, 2027.
25. E. Cances, B. Mennuchi, J. Tomassi, *J. Chem. Phys.*, 1997, **107**, 3032.
26. V. Barone, M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995.
27. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa,

M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision B.03*, Gaussian, Inc., Pittsburgh (PA), 2003.

28. A. S. Mendkovich, V. N. Leibzon, L. V. Martynova, *Elektrokhimiya*, 1982, **18**, 424 [*Sov. Electrochem.* (*Engl. Transl.*), 1982, **18**].
29. A. S. Mendkovich, M. A. Syroeshkin, L. V. Mikhal´chenko, A. I. Rusakov, V. P. Gul´tyai, *Izv. Akad. Nauk, Ser. Khim.*, 2008, 1463 [*Russ. Chem. Bull.*, *Int. Ed.*, 2008, **57**, 1492].
30. M. A. Syroeshkin, A. S. Mendkovich, L. V. Mikhal´chenko, A. I. Rusakov, V. P. Gul´tyai, *Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 459 [*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 468].
31. A. Chatterjee, *J. Chem. Sci.*, 2005, **117**, 533.
32. V. Pilepic, S. Ursic, *J. Mol. Struct. (THEOCHEM)*, 2001, **538**, 41.
33. P. Thanikaivelan, J. Padmanabhan, V. Subramanian, T. Ramasami, *Theor. Chem. Acc.*, 2002, **107**, 326.
34. J. Olah, C. Van Alsenoy, A. B. Sannigrahi, *J. Phys. Chem. A*, 2002, **106**, 3885.
35. F. A. Bulat, E. Chamorro, P. Fuentealba, A. Toro-Labbe, *J. Phys. Chem. A*, 2004, **108**, 342.
36. P. Jaramillo, P. Pérez, P. Fuentealba, S. Canuto, K. Coutinho, *J. Phys. Chem. B*, 2009, **113**, 4314.
37. K. Fukui, *Science*, 1982, **218**, 747.
38. M. A. Syroeshkin, M. N. Mikhailov, A. S. Mendkovich, A. I. Rusakov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 41 [*Russ. Chem. Bull.*, *Int. Ed.*, 2009, **58**, 41].
39. R. S. Ruoff, K. M. Kadish, P. Boulas, E. C. M. Chen, *J. Phys. Chem.*, 1995, **99**, 8843.

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