Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 129 (2008) 222–225
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Electron affinity and redox potential of tetrafluoro-*p*-benzoquinone: A theoretical study

Mansoor Namazian [a,*], Samira Siahrostami [b,1], Michelle L. Coote [a,*]

[a] *ARC Centre of Excellence for Free-Radical Chemistry and Biotechnology, Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia*
[b] *Department of Chemistry, Yazd University, P.O. Box 89195-741, Yazd, Iran*

Received 25 October 2007; received in revised form 15 November 2007; accepted 19 November 2007
Available online 23 November 2007

Abstract

The electron affinity of tetrafluoro-*p*-benzoquinone (2.69 eV) and the mono- (2.10 eV), 2,3-di- (2.29 eV), 2,5-di- (2.28 eV), 2,6-di- (2.31 eV) and tri- (2.48 eV) fluoro derivatives of *p*-benzoquinone have been calculated via standard ab initio molecular orbital theory at the G3(MP2)-RAD level of theory. Comparison of calculated electron affinities with the available experimental values shows excellent agreement between theory and experiment. The reduction potential of tetrafluoro-*p*-benzoquinone in acetonitrile vs. SCE (−0.03 V) has been calculated at the same level of theory and employing a continuum model of solvation (CPCM), and is also in excellent agreement with the experimental value (−0.04 V vs. SCE).

Keywords: G3(MP2)-RAD; Tetrafluoro-*p*-benzoquinone; CPCM; Reduction potential

1. Introduction

Tetrafluoro-*p*-benzoquinone (TFBQ), which has many applications in chemical synthesis, has aroused much interest [1–5]. Comparing with *p*-benzoquinone (BQ), the four fluorine substituents make a substantial difference to its behaviour. In particular, the fluorine atoms in TFBQ render the unsaturated carbon atoms carrying them more electropositive than usual; hence TFBQ is much easier to reduce than BQ, both in both the gas and solution phases. A difference of as much as 500 mV in the reduction potential of TFBQ compared to BQ in the non-aqueous solution of acetonitrile has been reported experimentally [6]. A significant difference has also been observed in electron affinities of TFBQ and BQ in the gas phase [7,8].

The accurate calculation of electron affinities and redox potentials is important both in chemistry and biochemistry and plays an important role in explaining the nature of electron-transfer reactions. Recently, we proposed an accurate method for the calculation of the one-electron reduction potentials in non-aqueous solution in which high-level composite methods for the gas-phase energies are combined with a continuum model of solvation. When assessed for a set of thirteen *p*-quinones (including the substituents CH_3, NH_2, Cl and CN) in the non-aqueous solution of acetonitrile, the mean absolute deviation of calculated reduction potential from the experiment was just 0.07 V [9]. However, since modelling of fluorine-substituted compounds can sometimes be problematic [10], it is of interest to determine whether the same level of accuracy can be achieved for the study of TFBQ.

In the present work, we describe the theoretical calculation of the electron affinity and redox potential of tetrafluoro-*p*-benzoquinone in acetonitrile using a reliable high-level composite method of ab initio calculations as well as a continuum model of solvation. Comparing the theoretical values with available experimental data, we demonstrate excellent agreement between theory and experiment. We also study the effect of fluorine substitution on the electron affinity for various mono-, di- and trisubstituted derivatives of *p*-benzoquinone.

---

* Corresponding authors.
E-mail addresses: namazian@rsc.anu.edu.au (M. Namazian), mcoote@rsc.anu.edu.au (M.L. Coote).

[1] Present address: Shiraz University, Shiraz, Iran.

0022-1139/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2007.11.007

2. Calculation of electron affinity and electrode potential

In an aprotic solvent, TFBQ undergoes a one-electron reduction reaction via equation (1) [6],

$$\mathrm{TFBQ(soln)} + \mathrm{e}^-(\mathrm{g}) \rightarrow \mathrm{TFBQ}^-(\mathrm{soln}) \tag{1}$$

where soln and g denote solution phase and gas phase, respectively. The total change in the Gibbs free energy of reaction (1), $-\Delta G^\circ$(soln), is related to the absolute reduction potential, E°, via equation (2) [11,12],

$$E^\circ = \frac{-\Delta G^\circ(\mathrm{soln})}{nF} \tag{2}$$

where n is the number of electrons transferred ($n = 1$ in this case) and F is the Faraday constant (96,485 C mol^{-1}). In the present work, we use an isodesmic method to calculate the relative reduction potentials so as to maximise the potential for systematic error cancellation [12,13]. The total free energy of reaction in the solution phase, ΔG°(soln), was calculated for the isodesmic isogyric reaction (3); analogous reactions were considered for the mono-, di- and trifluorinated species.

$$\mathrm{TFBQ(soln)} + \mathrm{BQ}^-(\mathrm{soln}) \rightarrow \mathrm{TFBQ}^-(\mathrm{soln}) + \mathrm{BQ(soln)} \tag{3}$$

ΔG°(soln) for this reaction was in turn calculated from the gas-phase free energies and free energies of solvation in acetonitrile of the reactants and products in the usual manner. The standard reduction potential, E°, of TFBQ vs. SCE (Standard Calomel Electrode) was then calculated from ΔG°(soln), and the redox potential of *p*-benzoquinone, E°(BQ) via equation (4),

$$E^\circ(\mathrm{TFBQ}) = \frac{-\Delta G^\circ(\mathrm{soln})}{nF} + E^\circ(\mathrm{BQ}) \tag{4}$$

where E°(BQ) is −0.52 V vs. SCE [6].

3. Computational methods

Standard ab initio molecular orbital theory [14] and density functional theory calculations [15] were carried out using the Gaussian 03 [16] and Molpro 2000.6 [17] software. Geometries of all species were optimized at the B3-LYP/6-31G(d) level of theory. The nature of each stationary point was established via B3-LYP-6-31G(d) frequency calculations. The Gibbs free energy of each species was calculated using single-point energies obtained at the G3(MP2)-RAD level of theory [10]. This high-level composite procedure, which was designed especially for the prediction of reliable thermochemistry for free radicals, uses additivity approximations to obtain CCSD(T) calculations with a large triple-ζ basis set. The principal features of the G3(MP2)-RAD procedure include the use of B3-LYP/6-31G(d) geometries, the use of URCCSD(T)/6-31G(d) as the highest-level correlation method and the use of ROMP2 to approximate basis-set-extension effects. The zero-point energies, thermal corrections and entropies have been calculated at B3-LYP/6-31G(d) level of theory under the harmonic oscillator/rigid rotor approximation; all frequencies were scaled by their recommended scale factors [18]. The G3(MP2)-RAD level of theory has been demonstrated to provide an accuracy of 4–5 kJ/mol when assessed against large test sets of thermochemical data [10].

In order to calculate solvation energies, a continuum model of solvation, the Conductor-like Polarizable Continuum Model (CPCM) [19], has been used at the recommended level of theory, B3-LYP/6-31 + G(d) [20]. The radii of the United Atom topological model applied on radii optimized for the DFT level of theory (UAKS), have been chosen for solvation energies as recommended. All geometries of the studied species have been optimized fully in the presence of solvent.

4. Results and discussion

4.1. Electron affinity and reduction potential of TFBQ

Table 1 shows the enthalpies of TFBQ and TFBQ^-, which have been calculated at G3(MP2)-RAD level of theory. Using these enthalpies, the calculated electron affinity of TFBQ is 2.69 eV. This theoretical value is in excellent agreement with experimental value of 2.70 ± 0.10 eV, as reported by Heinis et al. [8], which further supports G3(MP2)-RAD as a successful method for the calculation of energies where radicals are involved. By comparing the electron affinity of TFBQ with BQ (1.86 eV) [7], one can conclude that four fluorine atoms increase substantially the electron affinity by 0.8 eV (or 77 kJ/mol).

Table 1 also presents the solvation energies of TFBQ and TFBQ^- in acetonitrile, calculated using the B3-LYP/6-31 + G(d) level of theory. While the solvation energy of TFBQ (2.93 kJ/mol) is small, the solvation energy of the radical anion TFBQ^- (−159.91 kJ/mol) is quite large, as the solvent helps to stabilize the negative charge. However, the solvation energy of TFBQ^- is smaller than the solvation energy of BQ^-, −195.31 kJ/mol. This is because of the increased the volume of the ion and therefore the increased cavity space required to accommodate the solute. The cavitation energy is always positive and work is always required for this component of solvation. As Table 1 shows, the cavitation energies for TFBQ^- and BQ^- are 70.92 and 51.97 kJ/mol, respectively. The larger volume of the TFBQ^- anion compared with BQ^-, makes the charge density of the ion smaller and therefore the electrostatic interactions become smaller. The electrostatic energies of TFBQ^- and BQ^- are −183.59 and −207.44 kJ/mol, respectively.

Using the gas-phase and solvation energies of the species studied (Table 1), the total change of Gibbs energy of reaction (3), ΔG°(soln), is −422.8 kJ/mol, and hence the reduction potential of TFBQ is −0.03 V vs. SCE. This value is also in excellent agreement with the experimental value of −0.04 V [6] with a deviation of only 0.01 V.

The effect of fluorine atoms on the electron affinity and reduction potential can be understood through an examination of the charge distribution in the anions. We have calculated these charges using the natural bond orbital (NBO)

Table 1
Energy, enthalpy, entropy and Gibbs free energy of TFBQ and its radical anion, TFBQ$^-$, calculated at G3(MP2)-RAD level of theory at 298 K, together with B3-LYP/6-31 + G(d) CPCM solvation energies

	BQ [9]	BQ$^-$ [9]	TFBQ	TFBQ$^-$
Gas-phase energies				
E (kJ/mol)	−1000069.6	−1000255.4	−2041381.8	−2041641.3
H (kJ/mol)	−1000050.7	−1000237.2	−2041353.3	−2041613.0
S (J/mol)	331.8	331.6	410.8	411.8
G (kJ/mol)	−1000149.7	−1000336.1	−2041475.8	−2041735.8
EA (eV)	1.83	–	2.69	–
Solvation energies				
Cavitation energy (kJ/mol)	52.59	51.97	70.92	70.96
Dispersion energy (kJ/mol)	−48.45	−50.29	−55.77	−55.81
Repulsion energy (kJ/mol)	9.00	10.46	8.08	8.58
Total non-electrostatic (kJ/mol)	13.14	12.13	23.18	23.68
Total electrostatic (kJ/mol)	−19.25	−207.44	−20.25	−183.59
G(solv.)	−6.11	−195.31	2.93	−159.91
E° (vs. SCE) (V)			−0.03	

Calculated electron affinity (EA) and reduction potential (E°) for TFBQ are also included.

method at the level of B3-LYP/6-311 + G(3df,2p) [21]. For p-benzoquinone radical anion, the natural charge on each oxygen is −0.69, the charge on each of the carbon atoms connected directly to the oxygens (i.e., carbon atoms 1 and 4) is +0.35 and on each of the four other carbon atoms is −0.27 as shown in Fig. 1. Therefore, the negative charge is localized merely on oxygen and carbon atoms. For TFBQ$^-$, the natural charge on each oxygen is slightly reduced to −0.64 and each fluorine has a charge of −0.35. The fluorine substituents help to stabilize the negative charge of the reduced species, resulting in the high electron affinity of TFBQ. Interestingly, when we compare the reduction potential of TFBQ with that of the chlorine-substituted analogue, tetrachloro-p-benzoquinone (−0.005 V vs. SCE) [22], we find that the latter species is slightly easier to reduce, despite the reduced electronegativity of Cl vs. F. This is also observed in the gas phase; the electron affinity of tetrachloro-p-benzoquinone is 2.78 [8], which is also higher than that of TFBQ. It thus clear that the size of the substituents (H < F < Cl) also plays a role.

4.2. Electron affinity of mono-, di- and trifluoro-p-benzoquinone

In order to investigate the effect of each fluorine atom on electron affinity of BQ, we have also calculated the electron affinity of p-benzoquinone derivatives with one, two and three fluorine atoms using the G3(MP2)-RAD method. The effect of the number of fluorine atoms on the electron affinity is also shown in Fig. 2. The electron affinity of BQ with no fluorine atom, has been calculated as 1.93 eV and the experimental value is 1.86 eV with a 0.07 eV deviation [9]. The electron affinity of monofluoro-, 2,5-difluoro-, trifluoro- and tetrafluoro-p-benzoquinone are shown in Table 2. Inspection of these values reveals a strong linear correlation ($R^2 = 0.998$) between electron affinity and the number of fluorine atoms, with each additional fluorine atom increasing the electron affinity by 0.2 eV (see Fig. 2). For the disubstituted derivative, there are three different isomers, 2,3- 2,5- and 2,6-difluoro-p-benzoquinone. The calculated electron affinities for these species are within 0.03 eV of one another, which indicates that the positions

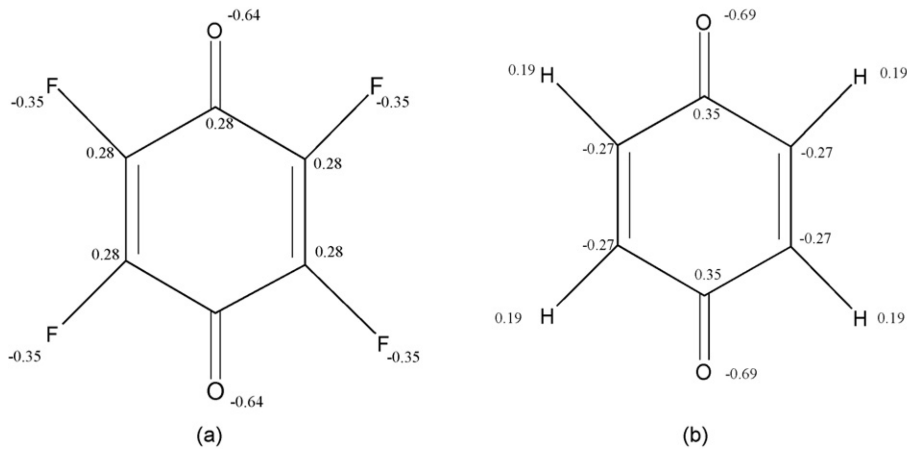

Fig. 1. NBO charges of (a) TFBQ$^-$ and (b) BQ$^-$.

Table 2
Enthalpy (*H*), entropy (*S*) and Gibbs free energy (*G*) of fluoro-, difluoro- and trifluoro-*p*-benzoquinone and their radical anions together with electron affinity (EA), calculated at G3(MP2)-RAD level of theory at 298 K

Compound		*H* (kJ/mol)	*S* (J/mol K)	*G* (kJ/mol)	EA (eV)
Fluoro-	Neutral	−1260388.9	350.3	−1260493.3	2.10
	Radical anion	−1260591.2	350.7	−1260695.8	
2,5-Difluoro-	Neutral	−1520725.0	369.1	−1520835.1	2.28
	Radical anion	−1520944.7	370.0	−1521055.0	
2,3-Difluoro-	Neutral	−1520708.0	370.9	−1520818.6	2.29
	Radical anion	−1520928.8	371.0	−1521039.4	
2,6-Difluoro-	Neutral	−1520722.6	369.4	−1520832.8	2.31
	Radical anion	−1520945.8	370.0	−1521056.1	
Trifluoro-	Neutral	−1781040.0	389.6	−1781156.2	2.48
	Radical anion	−1781279.4	390.5	−1781395.8	

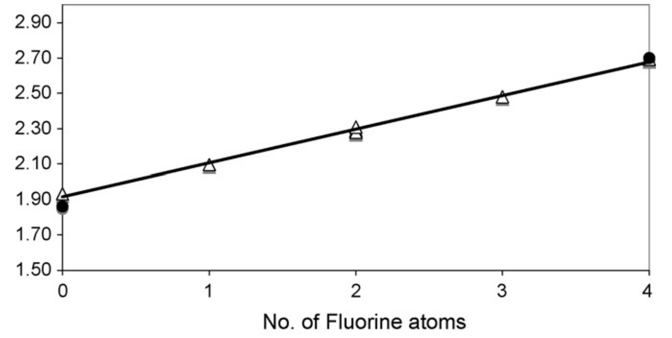

Fig. 2. Calculated (▲) and experimental (●) electron affinities of substituted *p*-benzoquinone vs. number of fluorine atoms. The line shows the relation between EA and the number of fluorine atoms, n_F (EA = 0.19 n_F + 1.92; $R^2 = 0.998$).

of fluorine atoms do not play a significant role in determining their stabilizing effect.

Supporting information available

B3-LYP/6-31G(d) optimized geometries in the form of GAUSSIAN archive entries, and corresponding total energies.

Acknowledgements

We gratefully acknowledge generous allocations of computing from the Australian Partnership for Advanced Computing and the Australian National University Supercomputing Facility, and financial support from the Australian Research Council under their Centres of Excellence program.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2007.11.007.

References

[1] M. Hudlicky, H.M. Bell, J. Fluorine Chem. 4 (1974) 149–157.
[2] F. Pichierri, A. Sekine, T. Ebisuzaki, Chem. Phys. 264 (2001) 9–19.
[3] V.E. Platonov, A. Haas, M. Schelvis, M. Lieb, K.V. Dvornikova, I.I. Osina, Yu.V. Gatilov, J. Fluorine Chem. 109 (2001) 131–139.
[4] E. Nield, J.C. Tatlow, Tetrahedron 8 (1960) 38–41.
[5] R. Marshall Wilson, J. Org. Chem. 48 (1983) 707–711.
[6] C.K. Mann, K.K. Barnes, Electrochemical Reactions in Nonaqueous Systems, Marcel Dekker, Inc., New York, 1970, pp. 190–195.
[7] NIST Chemistry WebBook, NIST Standard Reference Database, Number 69, June 2005 Release, http://webbook.nist.gov/chemistry/.
[8] T. Heinis, S. Chowdhury, S.L. Scott, P. Kebarle, J. Am. Chem. Soc. 110 (1988) 400.
[9] M. Namazian, M.L. Coote, J. Phys. Chem. A 111 (2007) 7227–7232.
[10] D.J. Henry, M.B. Sullivan, L. Radom, J. Chem. Phys. 118 (2003) 4849–4860.
[11] P.W. Atkins, Physical Chemistry, Oxford University Press, Oxford, 1999.
[12] M. Namazian, H.A. Almodarresieh, M.R. Noorbala, H.R. Zare, Chem. Phys. Lett. 396 (2004) 424–427.
[13] M. Namazian, H.R. Zare, Electrochim. Acta 50 (2005) 4350–4355.
[14] W.J. Hehre, L. Radom, P.V.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.
[15] R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1986.
[16] 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-Lahm, 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 C.02, Gaussian, Inc., Wallingford, CT, 2004.
[17] H.-J. Werner, P.J. Knowles, R.D. Amos, A. Bernhardsson, A. Berning, P. Celani, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A.W. Lloyd, S.J. McNicholas, F.R. Manby, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schutz, H. Stoll, A.J. Stone, R. Tarroni, T. Thorsteinsson, MOLPRO 2000.6, University of Birmingham, Birmingham, 1999.
[18] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502–16513.
[19] V. Barone, M. Cossi, J. Phys. Chem. A 102 (1998) 1995–2001.
[20] Y. Takano, K.N. Houk, J. Chem. Theory Comput. 1 (2005) 70–77.
[21] J.T. Nelson, W.J. Pietro, Inorg. Chem. 28 (1989) 544–548.
[22] K. Sasaki, T. Kashimura, M. Ohura, Y. Ohsaki, N. Ohta, J. Electrochem. Soc. 137 (1990) 2437–2443.