Supplemental Material

Halide ion effect on the ^1H NMR chemical shifts of the residual protons in commonly-employed deuterated solvents with tetra-*n*-butylammonium salts- Part 2

Yousif Assiri, Shofiur Rahman and Paris Elias Georghiou*

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland and Labrador, Canada, A1B3X7

Email: parisg@mun.ca

Table of Contents

	<u>Page</u>
Computational Studies	S2
Figure S1: Ball-and-stick structures of the complexes of TBACl with dichloromethane; chloroform and acetonitrile	S2
Figure S2: Ball-and-stick structures of the complexes of TBACl with Acetone, methanol and dimethyl sulfoxide	S3
Table 1: Calculated distances for selected parameters of the complexes of TBACl with dichloromethane; chloroform and acetonitrile	S4
Table 2: Calculated distances for selected parameters of the complexes of TBACl with acetone; methanol and dimethyl sulfoxide	S4
Table 3: Calculated binding energies (KJ/mole) for the TBACl with solvents	S5
Figure S3: Least-squares linear regression plot for the acetone- d_6 with TBACl determined by ^1H NMR titration	S5
Figure S4: Least-squares linear regression plot for the methanol- d_4 with TBACl determined by ^1H NMR titration	S4
Figure S5: Least-squares linear regression plot for the DMSO- d_6 with TBACl determined by ^1H NMR titration	S6
Figure S6: Least-squares linear regression plot for the dichloromethane- d_2 with TBACl determined by ^1H NMR titration	S6
Figure S7: Least-squares linear regression plot for the acetonitrile- d_3 with TBACl determined by ^1H NMR titration	S7
Reference	S7

Computational study

In order to try to better understand the contrasting chemical shift changes observed, a limited computational study was conducted using 1:1 complexes of TBACl with each of the solvents (in their non-deuterated forms) tested. The individual structures in the gas-phase were initially fully geometry-optimized using Gaussian 09¹ with the wB97xD level of DFT and the 6-31G(d) basis set and subsequently using the corresponding solvent corrections.

The lowest-energy 1:1 complex formed between a TBACl and dichloromethane molecule, for example, as shown in Figure S1 suggests a possible explanation for the down-field shifts observed. The shortest distance between the chloride anion, which is clearly situated close to the quaternary nitrogen, and the protons of the dichloromethane molecule is 2.443 Å. For the 1:1 complex of TBACl with acetonitrile, the corresponding distance is 2.610 Å. For the corresponding chloroform complex, the distance is 2.280 Å. The data are summarized in Table 1.

Figure S1. The geometry-optimized (ball-and-stick) structure of TBACl with chloroform (*left a*); dichloromethane (*middle b*) and acetonitrile (*right c*). Colour code: Cl⁻ = light green and nitrogen = blue.

For the solvents which showed up-field chemical shift changes for the residual protons, namely acetone- d_6 , methanol- d_4 and DMSO- d_6 the corresponding distances determined computationally for the structures shown in Figure S2, are summarized in Table 2. Since the protons in each of the respective methyl groups are not stationary, the corresponding Cl^- to carbon atoms of their methyl groups are also included. For the 1:1 acetone TBACl "complex", the shortest methyl proton and carbon to Cl^- distances are 2.692 Å and 3.749 Å respectively. For the 1:1 methanol TBACl "complex" the shortest methyl proton and carbon to Cl^- distances are 3.086 Å and 4.121 Å, respectively. (The methanol hydroxyl proton is approximately 5.750 Å away from the Cl^- and is clearly in the shielding environments of the n -butyl groups. It should also be noted that a larger linear dependence on the chemical shift changes for the residual hydroxy proton than the methyl residual protons was obtained ($-452 \text{ Hz}\cdot\text{M}^{-1}$ vs $-411 \text{ Hz}\cdot\text{M}^{-1}$). For the corresponding 1:1 DMSO TBACl "complex", the shortest methyl proton and carbon to Cl^- distance is 2.758 Å and 3.750 Å, respectively, and as in the case with methanol, the methyl groups of DMSO are presumably similarly more influenced by the shielding environments of the n -butyl groups.

Figure S2. The geometry-optimized (ball-and-stick) structure of TBACl with acetone (*left a*); methanol (*middle b*) and dimethyl sulfoxide (*right c*). Colour code: Cl^- = light green, nitrogen = blue, oxygen = red and sulfur = yellow.

Table 1. The calculated distance for selected parameters for the Backbones of the complexes of TBACl with dichloromethane, chloroform and acetonitrile optimized at wB97xD/ 6-31G(d) level (Distance in Å).

Parameter	TBACl plus CH ₂ Cl ₂ Distance (Å)	Parameter	TBACl plus CHCl ₃ Distance (Å)	Parameter	TBACl plus CH ₃ CN Distance (Å)
Cl54- H58	2.443	Cl54-H58	2.280	Cl60-H57	2.610
Cl54- C55	3.520	Cl56-C55	3.374	Cl60-C56	3.708
Cl54-H52	2.752	Cl54-H52	2.682	Cl60- H13	2.723
Cl54- H25	2.579	Cl54-H25	2.574	Cl60- H52	2.682
Cl56-H6	3.023	Cl54-H37	2.655	Cl60- H40	2.817
Cl54- H37	2.750	Cl57-H34	3.271	N54- H53	2.842
Cl56- H38	2.931	Cl56-H38	2.892	N54-H53	2.842
Cl57-H34	3.256	Cl56-H6	3.089	N54- H12	2.733

Table 2. The calculated distance for selected parameters for the Backbones of the complexes of TBACl with acetone, methanol and DMSO optimized at wB97xD/ 6-31G(d) level (Distance in Å).

Parameter	TBACl plus Acetone Distance (Å)	Parameter	TBACl plus Methanol Distance (Å)	Parameter	TBACl plus DMSO Distance (Å)
Cl64-H57	2.692	Cl60-H58	3.086	Cl64-H59	2.758
Cl64-C56	3.749	Cl60-C56	4.121	Cl64-C56	3.750
O54-H12	2.437	O55-H12	2.304	Cl64-H40	2.553
Cl64-H40	2.669	Cl60-H52	2.660	Cl64-H13	3.133
Cl64-H52	2.692	Cl60-H13	2.729	Cl64-H52	2.958
O54-H53	2.722	Cl60-H40	2.807	O54-H52	2.471
Cl64-H13	2.879	Cl60-H57	4.710	O54-H48	2.818
O54-H52	2.896	Cl60-H54	5.750	O54-H12	2.345
Cl64-H61	3.669			Cl64-H63	6.439

Calculated binding energies

The individual structures in the gas-phase were initially fully geometry-optimized using Gaussian 09⁴ with the wB97xD level of DFT and the 6-31G(d) basis set using the corresponding solvent corrections. The DFT wB97xD/6-31G(d) basis set-calculated binding energies (ΔE) of the TBACl complexes of the solvents (in their non-deuterated forms) formed between the TBACl and the free solvents in the corresponding solvent system at 298 K are based on the equation (1), and the results are summarized in in Table 3.

For this system, the binding energy ΔE can be express as follows:

$$\Delta E = (TBACl:Solvent)_{\text{complex}} - E(TBACl_{\text{free}}) - E(Solvent_{\text{free}}) \dots \dots \dots (1)$$

Table 3. Calculated binding energies (KJ/mole) for the TBACl with solvents (non-deutrated).

Host	Binding energies (KJ/mole) for TBACl with Solvents (non-deutrated)					
	Acetone	Methanol	DMSO	Acetonitrile	Dichloromethane	Chloroform
TBACl	-20.22	-24.58	-30.09	-29.29	-29.75	-40.56

Figure S3. Least-squares linear regression plot for the acetone-d₆ with TBACl determined by ¹H NMR titration.

Figure S4. Least-squares linear regression plot for the methanol- d_4 with TBACl determined by 1H NMR titration.

Figure S5. Least-squares linear regression plot for the DMSO- d_6 with TBACl determined by 1H NMR titration.

Figure S6. Least-squares linear regression plot for the acetonitrile- d_3 with TBACl determined by 1H NMR titration.

Figure S7. Least-squares linear regression plot for the dichloromethane-*d*₄ with TBACl determined by ¹H NMR titration.

Reference

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr. J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision D.01*; Gaussian, Inc., Wallingford CT, 2013.