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Application of high-resolution electrospray mass spectrometry for the elucidation of the disproportionation reaction of iodobenzene diacetate

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ABSTRACT

Disproportionation reactions take place in solution of (diacetoxyiodo)benzene (DIB) in acetonitrile in the presence of water, giving iodine(V) and iodine(I) species. This redox reaction is accelerated by the presence of water and by increasing the temperature. Several species of the solution of DIB were identified by high-resolution ESI-MS/MS, which allowed the elucidation of the mechanisms of disproportionation for DIB in gas phase and in solution. Key species in the process are the dimers $[PhI(OH)OIPh]^+$ at *m*/*z* 440.8864, $[PhI(OAc)OIPh]^+$ at *m*/*z* 482.8947, and $[PhI(O)(OAc)OIPh]^+$ at *m*/*z* 498.8887.

1. Introduction

Hypervalent iodine compounds constitute a useful class of reagents that can be used for several transformations. Most of these reactions occur cleanly in high level of selectivity, avoiding the use of toxic heavy metals [1]. Although hypervalent iodine(III) reagents have been intensively used in the last years, information regarding their properties in solution are not completely understood. Richter et al. [2] described that in the dissolution of [hydroxy(tosyloxy)iodo]benzene (PhI(OTs)OH, HTIB or Koser's Reagent) or of [hydroxy(mesyloxy)iodo]benzene (HMIB) in water at pH > 4.3 dissociation proceed under formation of the solvated iodonium ion $[PhIOH]^+$, as well as dimerization reactions giving species, such as $Ph(OH)I–O–I^+(OH_2)Ph$. Furthermore, this dimeric iodine(III) species undergoes a thermally induced disproportionation reaction giving PhI and $PhIO_2$, as a white precipitate. This redox reaction has been mentioned in several papers [3]. However, the mechanism for this process has not been elucidated. Moreover, a panorama of the species in methanolic solutions of iodosylbenzene was given by Sam et al. [4] when the mass spectra of a solution of PhIO in MeOH was acquired using electrospray ionization mass spectrometry (ESI-MS). The most important feature of the spectrum is the three peaks with equivalent intensity at *m*/*z* 235, 455 and 501, which were assigned to $[PhIOMe]^+$, to $[PhIO+PhI^+OMe]$ and to $[PhI(OMe)_2+PhI^+OMe]$, respectively. Information related to the species present in solutions of $PhI(OAc)_2$ (diacetoxyiodo)benzene (DIB) and $PhI(O_2CCF_3)_2$ is even more scarce. Based on the work of Schardt and Hill [5] toward the preparation of iodobenzene dimethoxide from iodosylbenzene, it has been accepted that the reactive species in oxidations using $PhI(OAc)_2$ or PhIO in MeOH in the presence of KOH is $PhI(OMe)_2$ [1q]. Recently, Cerioni and Uccheddu [6] have proposed an ion pair structure for bis(acetoxy)iodoarenes, such as $PhI(OAc)_2$, based on their chemical shifts in ^{17}O and ^{13}C NMR.

Electrospray ionization mass spectrometry (ESI-MS) and electrospray ionization tandem mass spectrometry (ESI-MS/MS) have now become a well established method to detect and characterize species in solution, including short-lived reaction intermediates [7]. For these reasons, some groups used ESI-MS and ESI-MS/MS for the study of reactions promoted by hypervalent iodine [8].

Based on the above scenario, we herein present the characterization of the species present in solution of DIB and their reactions in gas phase, suggesting a mechanism of the disproportionation reactions that take place in solutions of DIB. The techniques used to achieve this goal were ESI-MS and ESI-MS/MS [9]. Considering that the chemical behavior of iodine(III) and of iodine(V) may be very different, the understanding of factors governing the disproportionation reaction is of great importance in the use of hypervalent iodine reagents.

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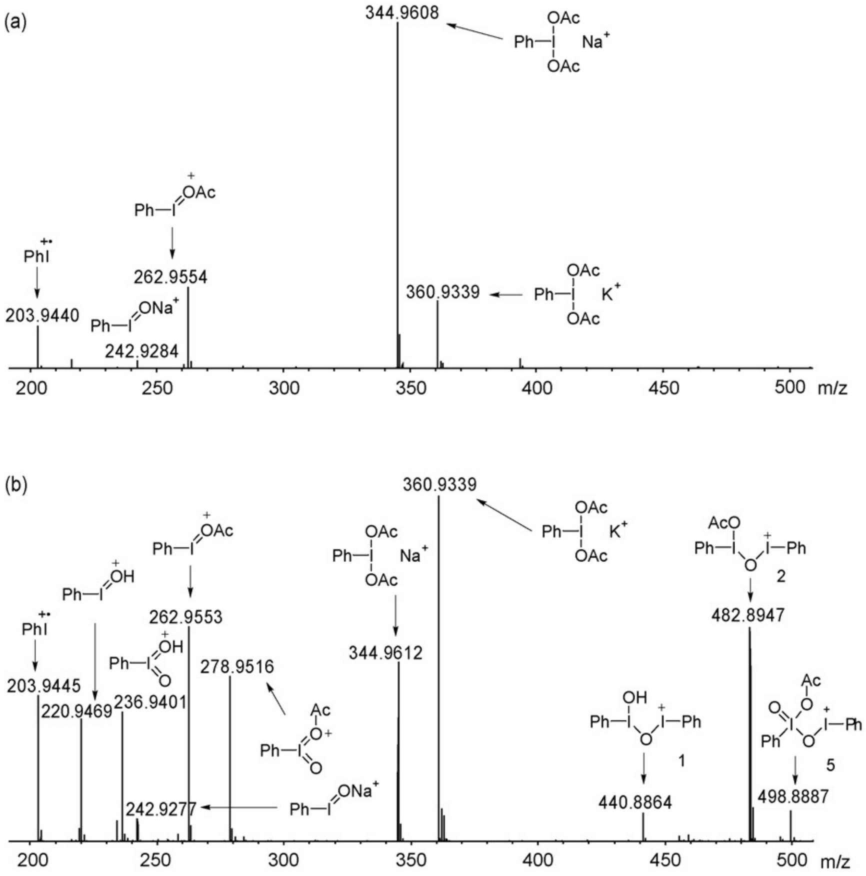


Fig. 1. Mass spectrum of a solution of $PhI(OAc)_2$ in CH_3CN at r.t.: (a) freshly prepared and (b) after 24 h.

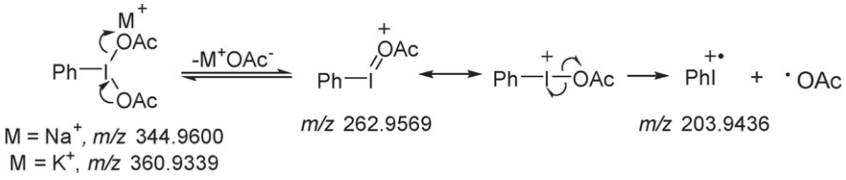
2. Experimental

DIB (98% from Acros) is commercially available and was used as received. The purity of the reagent was confirmed by NMR analysis (Bruker AC 200). Fresh solution of DIB in acetonitrile (HPLC grade, water content 0.001%) was prepared at 4.7 mmol L^{-1} and at pH 5. This solution was used at up to 10 min after preparation. “Old” DIB solution was prepared as previously mentioned and allowed to stand for 24 h. All mass spectra were acquired using an UltrOTOF Q quadrupole time of flight hybrid instrument (Bruker Daltonics, Billerica, MA, USA) mass spectrometer equipped with an ionspray interface. Samples were introduced using syringe pump and Hamilton syringes (Hamilton Co., Reno, NE). Fragment ion (tandem) mass spectra (MS/MS) were obtained by collision-induced dissociation of precursor ion selected by their m/z value using nitrogen as collision gas. The ESI-MS analyses were performed at the positive-ion mode.

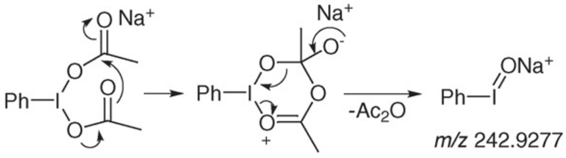
3. Results and discussion

The ESI-MS experiments were carried out using acetonitrile as solvent, because in this solvent disproportionation reactions are slow enough to track changes in composition of the solution by ESI-MS. In addition, acetonitrile does not form other species by nucleophilic attack on DIB, causing minimum interference. First, we decided to check if the disproportionation of DIB indeed take place in acetonitrile. Thus, a solution of DIB in acetonitrile was allowed to stand for 24 h and a white insoluble compound was then obtained. Direct comparison of this solid with an authentic sample of $PhIO_2$ indicated that disproportionation occurred. After this control experiment, the spectrum of a freshly prepared solution of DIB in acetonitrile was acquired, presenting as the main species the expected Na^+ and K^+ adducts $[PhI(OAc)_2Na]^+$, (obs. m/z 344.9608, calc. 344.9600, 2.3 ppm) and $[PhI(OAc)_2K]^+$, (obs. m/z 360.9339, calc. 360.9339, 0 ppm). Other important species were $[PhIONa]^+$ (obs. m/z 242.9284, calc. 242.9283, −0.42 ppm), $[PhIOAc]^+$ (obs. m/z 262.9554, calc. 262.9569, −5.7 ppm) and $[PhI]^{\bullet+}$ (obs. m/z 203.9440, calc. 203.9430, 4.9 ppm) (Fig. 1a).

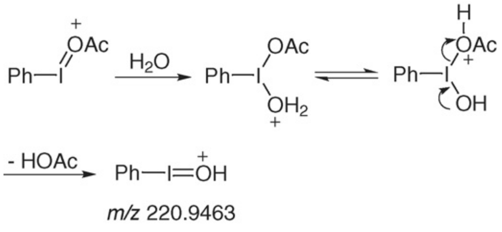
The cation radical $[PhI]^{\bullet+}$ would be generated by the source-mediated homolytic cleavage of the iodine–oxygen bond of $[PhIOAc]^+$ (Scheme 1) [10]. This hypothesis is sustained by the tandem mass spectrum of the cation $[PhIOAc]^+$ that generated exclusively the cation radical $[PhI]^{\bullet+}$ (see supplementary



Scheme 1.



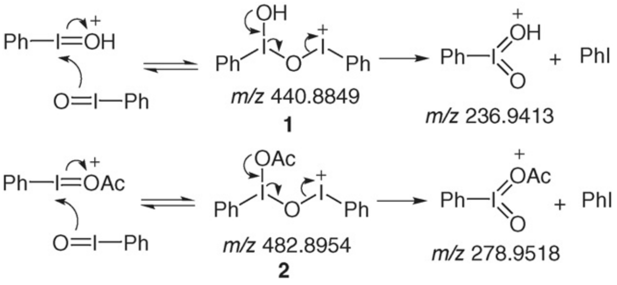
Scheme 2.



Scheme 3.

information). Finally, the ion $[PhIONa]^+$ would be formed by the exit of acetic anhydride from the ion $[PhI(OAc)_2Na]^+$ (Scheme 2).

Next, the solution of DIB in acetonitrile was allowed to stand at room temperature and a new mass spectrum was acquired in regular intervals. Comparing to the mass spectrum obtained from the fresh solution, a striking difference was observed only after 24 h. The mass spectrum of this “old” solution revealed the presence of species that were not detected in the fresh solution, including some iodine(V) species. As the conditions of the instrument were constant in the fresh and in the 24 h solutions and the only variation was the interval time, we can conclude that the disproportionation reaction occurs in solution over time (Fig. 1b). Among the detected iodine(V) species were $[PhI(O)OH]^+$ (obs. m/z 236.9401, calc. 236.9413, −5.1 ppm) and $[PhI(O)OAc]^+$ (obs. m/z 278.9516, calc. 278.9518, −0.7 ppm). The ion $[PhIOAc]^+$ appears in both spectra (fresh solution and after 24 h). Thus, it is not possible to define if this species could be formed in solution or by source dissociation of Na^+ and K^+ adducts of DIB. The ion $[PhIOAc]^+$ is also observed in the ESI-MS/MS experiments of $[PhI(OAc)_2Na]^+$ and of $[PhI(OAc)_2K]^+$ ions (see supplementary information) supports this proposition. One of the new iodine(III) species is $[PhIOH]^+$ (obs. m/z 220.9469, calc. 220.9463, 2.7 ppm), which could be formed by elimination of AcOH from the transient species $[PhI(H_2O)OAc]^+$, that would be originated from addition of water to $[PhIOAc]^+$. Thus, water plays an important role in the disproportionation of DIB (Scheme 3). The radical cation $[PhI]^{\bullet +}$ could also be generated by the homolytic cleavage of $[PhIOH]^+$ ion. Since the potential and other parameters were not modified from the fresh solution, the species $[PhIOH]^+$, $[PhI(O)OH]^+$, $[PhI(O)OAc]^+$, $[PhI(OH)OIPh]^+$, $[PhI(OAc)OIPh]^+$ and



Scheme 4.

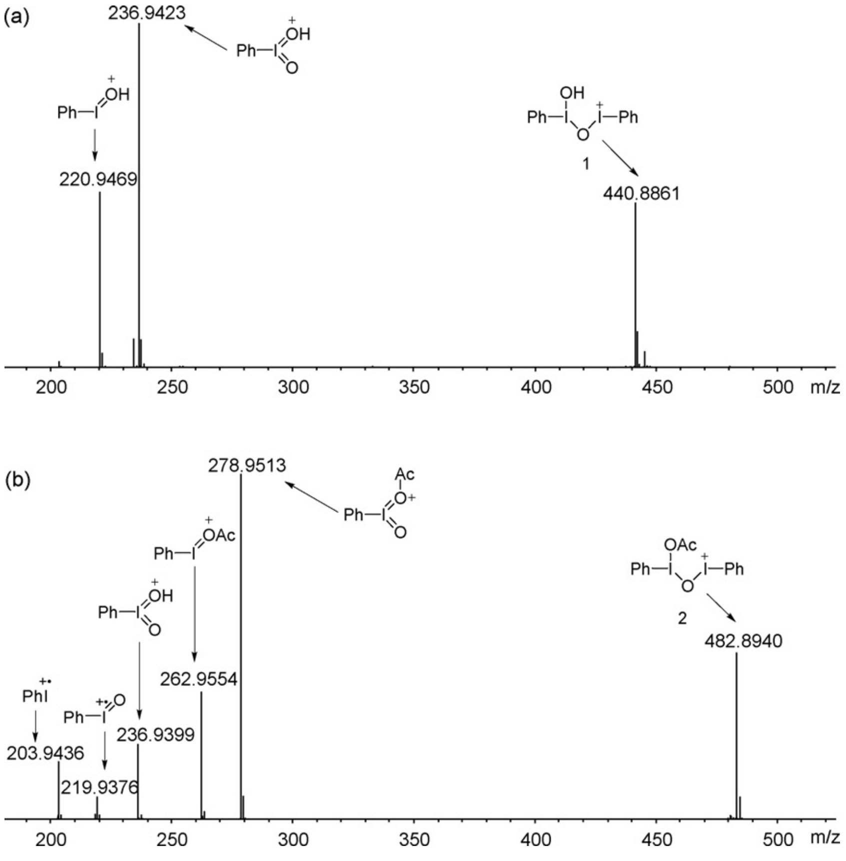


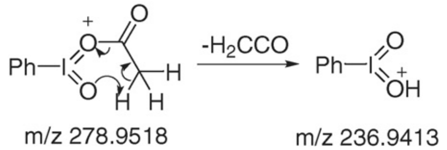
Fig. 2. ESI-MS/MS spectra of the dimers: (a) **1**, $[PhI(OH)OIPh]^+$; (b) **2**, $[PhI(OAc)OIPh]^+$.

$[PhI(O)(OAc)OIPh]^+$ must be formed and present in solution, except $[PhI]^{\bullet +}$, whose formation probably occurs at the source.

The dimeric species $[PhI(OH)OIPh]^+$ (**1**) (obs. *m*/*z* 440.8864, calc. 440.8849, 3.4 ppm) and $[PhI(OAc)OIPh]^+$ (**2**) (obs. *m*/*z* 482.8947, calc. 482.8954, −1.5 ppm) are also present in the solution of DIB after 24 h (Fig. 1b). These molecules are analogous to those characterized by Richter and are probably formed by reversible addition of iodosylbenzene, which is originated by deprotonation of $[PhIOH]^+$, to the cations $[PhIOH]^+$ and $[PhIOAc]^+$, respectively. Furthermore, considering the mechanism suggestion of Masson et al. [11], the dimers **1** and **2** could undergo a disproportionation giving each an iodine(V) and an iodine(I) species. These disproportionations would be entropically favored considering that two molecules are formed from the dimers **1** and **2** (Scheme 4).

To provide evidence in gas phase for the above sequence of reactions $[PhI(OH)OIPh]^+$ was selected for ESI-MS/MS analyses. For this group of experiments, we closed the collision gas entrance and turned off the collision gas energy. In this experiment, $[PhIOH]^+$ (obs. *m*/*z* 220.9469, calc. 220.9463, 2.7 ppm) was detected, which is evidence for the reversible formation of dimer **1**. Furthermore, the presence of protonated iodylbenzene at *m*/*z* 236.9423 (calc. 236.9413, 4.2 ppm) in the gas phase indicates that this iodine(V) species originates from dimer **1** (Fig. 2a). Thus, these data confirm the formation and the disproportionation of **1**. A similar pattern would be expected for a similar experiment with the dimer **2**. Indeed, when **2** was selected for an ESI-MS/MS experiment, $[PhI(O)OAc]^+$ (obs. *m*/*z* 278.9513, calc. 278.9518, −1.8 ppm) and $[PhIOAc]^+$ (obs. *m*/*z* 262.9554, calc. 262.9569, −5.7 ppm) were observed. Furthermore, $[PhI(O)OH]^+$ (obs. *m*/*z* 236.9399, calc. 236.9413, −5.9 ppm), $[PhIO]^{\bullet +}$ (obs. *m*/*z* 219.9376, calc. 219.9380, −1.8 ppm) and $[PhI]^{\bullet +}$ (obs. *m*/*z* 203.9436, calc. 203.9430, 2.9 ppm) were also detected (Fig. 2b).

The iodine(V) ion $[PhI(O)OAc]^+$ could be formed by the disproportionation of the dimer **2**. This dimer would also lead to $[PhIOAc]^+$ and to [PhIO], which is the reverse of the dimerization. Then, $[PhIOAc]^+$ could produce $[PhI]^{\bullet +}$, as previously shown (Scheme 1). Furthermore, loss of CH_2CO by $[PhI(O)OAc]^+$ would yield $[PhI(O)OH]^+$ (Scheme 5). Finally, homolytic cleavage of the I–O bond of $[PhI(O)OAc]^+$ would lead to $[PhIO]^{\bullet +}$, as proposed for $[PhI]^{\bullet +}$ in Scheme 1. The presence of both $[PhI(O)OH]^+$ and $[PhIO]^{\bullet +}$ ions in the tandem mass spectrum of $[PhI(O)OAc]^+$ (see supplementary information) supports this consideration. The higher fragmentation pattern of the dimer **2** $[PhI(OAc)OIPh]^+$ compared to dimer **1** $[PhI(OH)OIPh]^+$ could be explained by the stabilisation of radicals by AcO [10].



Scheme 5.

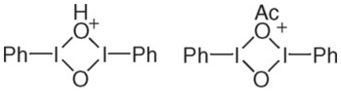


Fig. 3. Structure of the cyclic dimers **3** and **4**.

Although the dimers **1** and **2** are represented in an acyclic form, the analogous cyclic dimers **3** and **4** (Fig. 3), similar to that described by Ochiai et al. [12] cannot be rejected. An equilibrium between cyclic and acyclic forms appears to be possible. Arbitrarily, acyclic forms **1** and **2** are used in this paper.

Another species detected in the spectrum of 24-h old DIB solution in CH_3CN was $[PhI(O)(OAc)OIPh]^+$ (**5**) (obs. *m*/*z* 498.8887, calc. 498.8903, −3.2 ppm) (Fig. 1b), in which there are iodine(III) and iodine(V) atoms. The dimer **5**, when selected for ESI-MS/MS without induced collisions (no collision energy applied), yielded mainly $[PhIOAc]^+$ (obs. *m*/*z* 262.9539, calc. 262.9569, −16.7 ppm) and, presumably, $PhIO_2$ (Fig. 4). The presence of $[PhI]^{\bullet +}$ should be related with the fragmentation of the ion $[PhIOAc]^+$ already discussed (Scheme 1). This result gave us the final clue for the overall mechanism involved in the disproportionation reactions of DIB in acetonitrile.

Although the evidences for the formation and disproportionation of dimers **1** and **2** shown in Scheme 4 were obtained in gas phase, these reactions also occurs in solution considering that $PhIO_2$ was isolated from the solution of DIB in acetonitrile. Thus, the disproportionation reaction of DIB in solution takes place by two mechanisms: the first occurring via dimer **1** (Scheme 4), and the second via the cycle shown in Scheme 6 starting from $[PhIOAc]^+$, the only species in the cycle present in the fresh solution. This cation would react with PhIO giving the dimer **2**, which would disproportionate to PhI and $[PhI(O)OAc]^+$, as described in Scheme 4. The

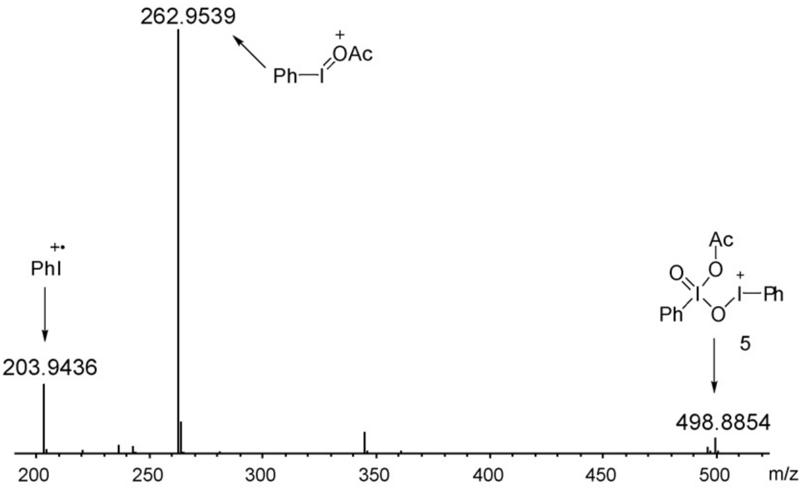
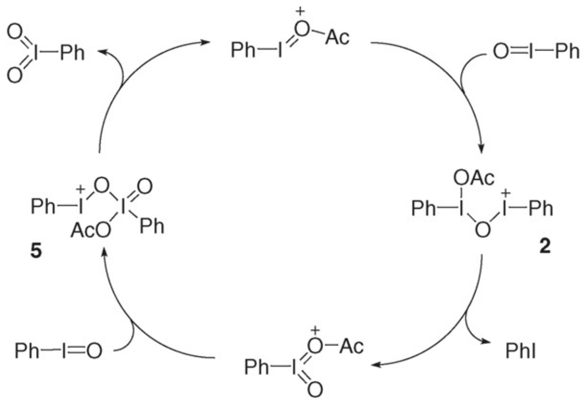
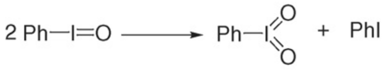


Fig. 4. ESI-MS/MS of the dimer **5**, $[PhI(O)(OAc)OIPh]^+$.



Scheme 6.



Scheme 7.

iodine(V) species $[PhI(O)OAc]^+$ would react with PhIO, giving the mixed dimer **5**. Finally, based on the ESI-MS/MS shown in Fig. 4, **5** would furnish $PhIO_2$ and $[PhIOAc]^+$, closing the cycle. Since the concentration of $[PhIOH]^+$ is smaller than that of $[PhIOAc]^+$, we consider that the formation of the dimer $[PhI(OAc)OIPh]^+$ would be faster than $[PhI(OH)OIPh]^+$. Indeed, this is observed in the mass spectrum of the solution of DIB, where the relative intensity of the peak related to $[PhI(OAc)OIPh]^+$ is higher than that associate to $[PhI(OH)OIPh]^+$ (Fig. 1b). In conclusion, the cycle shown in Scheme 6 is the main disproportionation pathway for DIB in acetonitrile. Overall, the cycle represents the consumption of two molecules of iodosylbenzene giving iodylbenzene and iodobenzene (Scheme 7). This agrees with the experimental observation, because the formation of iodylbenzene as a white solid was noted after 24 h.

The temperature is an important parameter in the kinetics of reactions, which could probably influence in the disproportionation of DIB [2,13]. Thus, a solution of DIB was rapidly prepared in acetonitrile at 80 °C and immediately injected in the mass spectrometer (Fig. 5). The spectrum thus obtained presents DIB adducts with Na^+ and K^+, as the most intense signals. Furthermore, the spectrum shows all the species found in the 24-h-old DIB solution (Fig. 1b), such as $[PhIOH]^+$ (obs. m/z 220.9448, calc. 220.94639, −6.8 ppm), $[PhIOAc]^+$ (obs. m/z 262.9552, calc. 262.9569, −6.5 ppm), $[PhI]^{\bullet+}$ (obs. m/z 203.9423, calc. 203.9430, −3.4 ppm), dimers **1** (obs. m/z 440.8862, calc. 440.8849, 3.0 ppm), **2** (obs. m/z 482.8967, calc. 482.8954, 2.7 ppm) and **5** (obs. m/z 498.8910, calc. 498.8903, 1.4 ppm), iodine(V) species $[PhI(O)OH]^+$ (obs. m/z 236.9395, calc. 236.9413, −7.6 ppm) and $[PhI(O)OAc]^+$ (obs. m/z 278.9501, calc. 278.9518, −6.1 ppm). Thus, the disproportionation reaction of DIB in solution of acetonitrile increases at higher temperature.

Considering the participation of H_2O in the formation of $[PhIOH]^+$, which has an important role in the disproportionation (Scheme 3), we decided to investigated the species present in solutions where a significant amount of water would be present during ESI-MS analyses. The first experiment was the acquisition of the ESI-MS of a freshly prepared solution of DIB in $CH_3CN:H_2O$ (1:1) (Fig. 6a). The spectrum of this solution is quite different from that in only acetonitrile (Fig. 1a). However, it resembles that of the 24-h-old solution of DIB (Fig. 1b), because the same species are observed, including those bearing the iodine at the oxidation state V. Thus, the presence of H_2O accelerates the disproportionation reaction. This effect could take place only in the mass spectrometer and not in the solution. Considering this hypothesis, the spectrum of DIB in CH_3CN/H_2O solution acquired shortly after the preparation of the solution should be somewhat similar to that of the freshly prepared solution. Nevertheless, ESI-MS after 1.5 h showed that signals related to the disproportionation reaction, such as the iodine(V) species $[PhI(O)OH]^+$ at m/z 236.9425 and $[PhI(O)OAc]^+$ at m/z 278.9542 have a higher relative intensity (50 and 70%, respectively) than in the fresh solution (Fig. 6b). This result confirms that water accelerates the disproportionation in solutions of DIB, because this solvent better stabilizes the cationic intermediates involved in the medium [2]. Furthermore, considering that the attack of a molecule of water is involved in the first step of the formation of iodosylbenzene (Scheme 3), increasing the concentration water would elevate the concentration of PhIO, favoring the formation of the $[PhIOH]^+$ that can forms the dimer **1** (Scheme 6). In agreement to that, the relative intensity of the signals corresponding to $[PhIOH]^+$ and to $[PhIOAc]^+$ are inverted in the spectra of the fresh solution when compared to that after 1.5 h. Nonetheless, the concentration of dimer **1** did not changed, because the very reactive dimer **1** would go immediately to the entropically favored disproportion reaction.

In an ESI-MS study, the presence of water could affect the ionization and/or redox processes, [14] which would have an influence in the disproportionation reaction, as discussed above. Considering that and to confirm the effect of the water in the disproportionation reaction [15], an additional experiment was performed. This time,

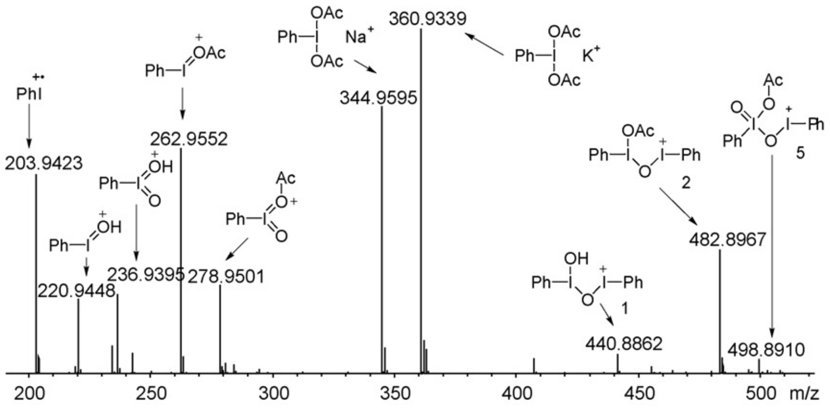


Fig. 5. ESI-MS of a freshly prepared solution of DIB in CH_3CN at 80 °C.

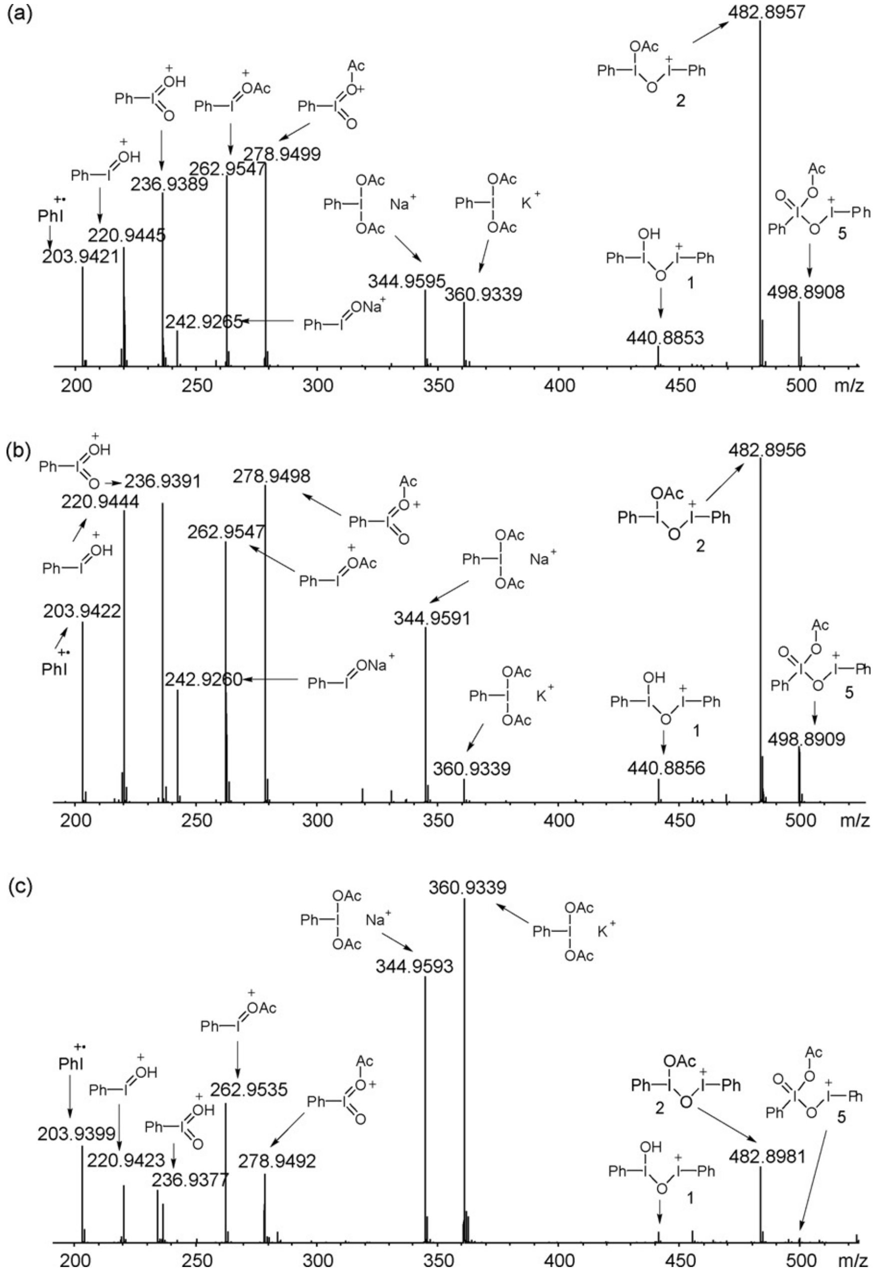


Fig. 6. ESI-MS of a solution of DIB at r.t.: (a) in CH_3CN/H_2O: freshly prepared; (b) in CH_3CN/H_2O: after 1.5 h; (c) in CH_3CN: source saturated with H_2O before the injection.

the source was saturated with water before the injection. Then, a fresh prepared solution of DIB in pure acetonitrile was injected. The spectrum thus obtained shows the presence of the characteristics species for the disproportionation reaction, namely the dimers **1** and **2**, as well as the iodine(V) species $[PhI(O)OH]^+$ and $[PhI(O)OAc]^+$ (Fig. 6c), in contrast to that performed without the presence of water in the source (Fig. 1a). In the presence of water, the spectrum is similar to that obtained with the 24 h old solution of DIB (Fig. 1b) and with that of the aqueous solution (Fig. 6c). Thus, water has a strong influence in the disproportionation reaction both in solution and on the machine. Considering that several reactions using iodine(III) reagents are performed using water as solvent and the different chemical behavior between iodine(V) and (III) [1], the influence of water in the disproportionation will be of great value to understand several reactions. Indeed, we believe that iodine(V) species are involved in some reactions using DIB in the presence of water.

4. Conclusions

Disproportionation reactions take place spontaneously in solution of DIB in acetonitrile giving iodine(V) and iodine(I) species. This redox reaction is accelerated by the presence of water and by increasing the temperature. Several species of the solution of DIB were identified in the solutions and evidences for their reactions in gas phase were obtained. These data gave us information to propose a mechanism for the disproportionation of DIB in solution. The mechanism features the presence of dimeric species, which were fully characterized.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2008.06.012.

References

[1] The chemistry related to hypervalent iodine compounds has been reviewed in a variety of forms. For some recent examples, see:
(a) M. Ochiai, Chem. Rec. 7 (2007) 12;
(b) U. Ladziata, V.V. Zhdankin, SYNLETT 527 (2007);
(c) L.F. Silva Jr., Molecules 11 (2006) 421;
(d) U. Ladziata, V.V. Zhdankin, ARKIVOC 9 (2006) 26;
(e) E.D. Matveeva, M.V. Proskurnina, N.S. Zefirov, Heteroatom. Chem. 17 (2006) 595;
(f) R.D. Richardson, T. Wirth, Angew. Chem. Int. Ed. 45 (2006) 4402;
(g) V.V. Zhdankin, Curr. Org. Synth. 2 (2005) 121;
(h) T. Wirth, Angew. Chem. Int. Ed. 44 (2005) 3656;
(i) R.M. Moriarty, J. Org. Chem. 70 (2005) 2893;
(j) H. Tohma, Y. Kita, Adv. Synth. Catal. 346 (2004) 111;
(k) T. Wirth, M. Ochiai, A. Varvoglis, V.V. Zhdankin, G.F. Koser, H. Tohma, Y. Kita, Topics in Current Chemistry, 224, Springer, Berlin, Heidelberg, 2003;
(l) P.J. Stang, J. Org. Chem. 68 (2003) 2997;
(m) V.V. Zhdankin, P.J. Stang, Chem. Rev. 102 (2002) 2523;
(n) H. Togo, K. Sakuratani, Syn. Lett. (2002) 1966;
(o) A. Varvoglis, Tetrahedron 53 (1997) 1179;
(p) A. Kirschning, Eur. J. Org. Chem. (1998) 2267;
(q) A. Varvoglis, Hypervalent Iodine in Organic Synthesis, Academic Press Inc., San Diego, 1996;
(r) G.F. Koser, Aldrichim. Acta 34 (2001) 89.

[2] H.W. Richter, B.R. Cherry, T.D. Zook, G.F. Koser, J. Am. Chem. Soc. 119 (1997) 9614.

[3] (a) C. Willgerodt, J. Prakt. Chem. 33 (1886) 154;
(b) M.S. Yusubov, K.W. Chi, J.Y. Park, R. Karimov, V.V. Zhdankin, Tetrahedron Lett. 47 (2006) 6305;
(c) A.Y. Koposov, R.R. Karimov, A.A. Pronin, T. Skrupskaya, M.S. Yusubov, V.V. Zhdankin, J. Org. Chem. 71 (2006) 9912.

[4] J.W. Sam, X.J. Tang, R.S. Magliozzo, J. Peisach, J. Am. Chem. Soc. 117 (1995) 1012.

[5] B.C. Schardt, C.L. Hill, Inorg. Chem. 22 (1983) 1563.

[6] G. Cerioni, G. Uccheddu, Tetrahedron Lett. 45 (2004) 505.

[7] For reviews, see:
(a) D. Fabris, Mass Spectrom. Rev. 24 (2005) 30;
(b) L.S. Santos, L. Knaack, J.O. Metzger, Int. J. Mass Spectrom. 246 (2005) 84.

[8] For some examples, see:
(a) Z. Li, Z.H. Tang, X.X. Hu, C.G. Xia, Chem. Eur. J. 11 (2005) 1210;
(b) M. Ochiai, K. Miyamoto, T. Suefuji, M. Shiro, S. Sakamoto, K. Yamaguchi, Tetrahedron 59 (2003) 10153;
(c) H. Tohma, T. Maegawa, S. Takizawa, Y. Kita, Adv. Synth. Catal. 344 (2002) 328.

[9] For a preliminary communication of part of this work, see:
L.F. Silva Jr., N.P. Lopes, Tetrahedron Lett. 46 (2005) 6023.

[10] (a) T. Dohi, K. Morimoto, N. Takenaga, A. Goto, A. Maruyama, Y. Kiyono, H. Tohma, Y. Kita, J. Org. Chem. 72 (2007) 109;
(b) H. Togo, Y. Hoshina, T. Muraki, H. Nakayama, M. Yokoyama, J. Org. Chem. 63 (1998) 5193;
(c) P.A. Evans, T.A. Brandt, J. Org. Chem. 62 (1997) 5321;
(d) T. Muraki, H. Togo, M. Yokoyama, Tetrahedron Lett. 37 (1996) 2441;
(e) H. Togo, M. Aoki, T. Kuramochi, M. Yokoyama, J. Chem. Soc., Perkin Trans. 1 (1993) 2417;
(f) H. Togo, M. Aoki, M. Yokoyama, Tetrahedron 49 (1993) 8241;
(g) H. Togo, M. Aoki, M. Yokoyama, Tetrahedron Lett. 32 (1991) 6559.

[11] I. Masson, E. Race, F.E. Pounder, J. Chem. Soc. (1935) 1669.

[12] M. Ochiai, M. Kida, K. Sato, T. Takino, S. Goto, N. Donkai, T. Okuyama, Tetrahedron Lett. 40 (1999) 1559.

[13] P. Kazmierczak, L. Skulski, L. Kraszkiewicz, Molecules 6 (2001) 881.

[14] A.E.M. Crotti, R. Vessecchi, J.L.C. Lopes, N.P. Lopes, Quim. Nova 29 (2006)287.

[15] N.P. Lopes, T. Fonseca, J.P.G. Wilkins, J. Staunton, P.J. Gates, Chem. Commun. (2003) 72.