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# Association and Dissociation of *(Z)*-(β-Bromoalkenyl)-(phenyl)iodonium Bromide in Chloroform Solution: Detection of Vinyl-$\lambda^3$-Iodane Dimer in Solution

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## Abstract

Formation of the iodonium ion **1a** as well as the dimer **3a** is found in chloroform solution of *(Z)*-(2-bromo-1-decenyl)(phenyl)iodonium bromide (**2a**) by vapor pressure osmometry and $^1$H NMR experiments, and the dissociation and association constants are determined. The dimer **3a** is also detected by FAB-MS in the gas phase.

*Keywords:* Hypervalent elements; Dimerization; NMR; Mass spectrometry

Cryoscopic and conductance measurements have shown extensive dissociation of $\lambda^3$-diaryliodanes ($Ar_2IX$: X = $BF_4$, Cl, Br, OAc) into iodonium ions in polar solvents such as $H_2O$, MeOH, and DMSO [1]. Even in dichloromethane, bis(4-methylphenyl)iodonium tetrafluoroborate dissociates into ions with dissociation constant $K_{dissoc} = 4.7 \times 10^{-6}$ M at 0 °C [1b]. On the other hand, bis(4-cyclohexylphenyl)iodonium iodide has been shown to largely exist as quadrupoles in benzene [2]. Recently, we found that in the presence of *n*-$Bu_4NCl$ the $\lambda^3$-vinylchloroiodane *(E)*-*t*-BuCH=CHI(Ph)Cl in chloroform solution yields the iodate *(E)*-*t*-BuCH=CHI$^-$(Ph)$Cl_2$ in addition to formation of the iodonium ion *(E)*-*t*-BuCH=CHI$^+$Ph, with the dissociation and association constants of $K_{dissoc} = 5.9 \times 10^{-5}$ M and $K_{assoc} = 6$ M$^{-1}$ at $\mu = 0.1$ [3]. We report herein vapor pressure osmometric and spectroscopic studies on the molecular association and dissociation of *(Z)*-(2-bromo-1-decenyl)(phenyl)iodonium bromide (**2a**) in chloroform solution, which suggest equilibrium formation of the dimer **3a** as well as the iodonium ion **1a**.

Evidence for the aggregation of the $\lambda^3$-vinylbromoiodane **2** to the dimeric form **3** was obtained from FAB mass spectrometry (FAB-MS). In the spectrum of FAB-MS (*m*-nitrobenzyl alcohol, glycerol matrix) of **2a**, in addition to the M$^+$ - Br peaks [*m/z* (rel intensity); 421 (100), 423 (98)], prominent peaks of 2×M$^+$ - Br [921 (6), 923 (18), 925 (18)] were observed. Furthermore, when a solution of a 1:1 mixture of *(Z)*-(2-bromo-1-decenyl)iodane **2a** and

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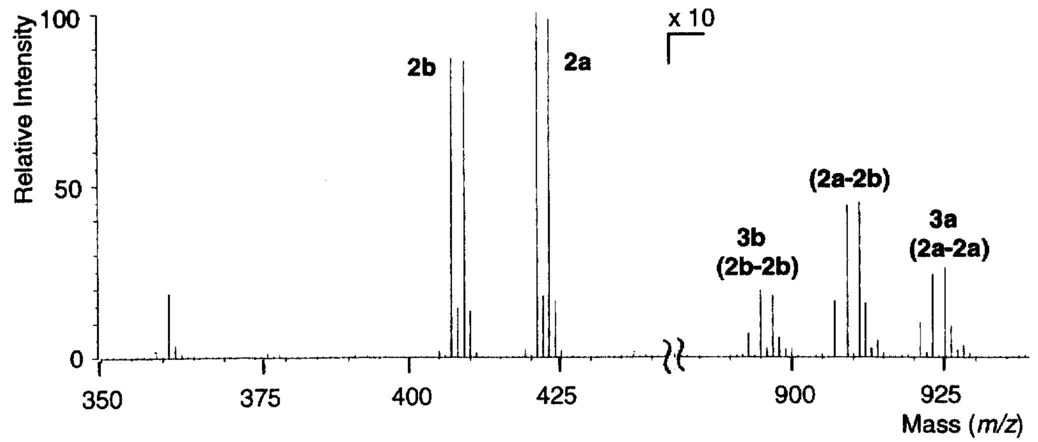
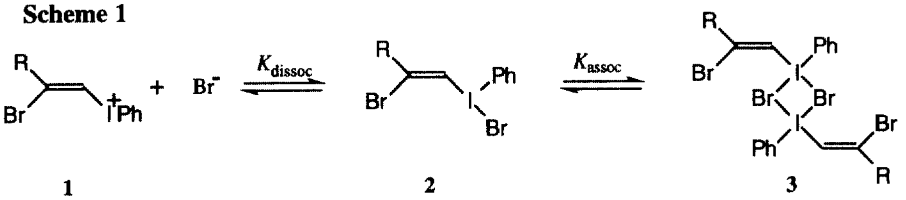


**Figure 1.** FAB mass spectra of a 1:1 mixture of **2a** and **2b**: homodimers **3a** and **3b**, and heterodimer **2a-2b**.

(*Z*)-(2-bromo-1-nonenyl)iodane **2b** was analyzed by FAB-MS, formation of a heterodimer (**2a-2b**) was clearly observed in addition to homodimers **3a** (**2a-2a**) and **3b** (**2b-2b**) (Figure 1). These results are indicative of dimeric structure **3** even in the gas phase, in which the strength of the coordination bonds in **3** is close to the scope of mass spectroscopy.

**Scheme 1**



**1** **2** **3**

**a**; R = $n$-$C_8H_{17}$, **b**; R = $n$-$C_7H_{15}$

The molecular weight of the $\lambda^3$-vinylbromoiodane **2a** in chloroform solution was determined by Corona vapor pressure osmometer with benzil as a standard at 25 °C. Vapor pressure osmometry of **2a** in chloroform at $1\times10^{-3}$ M gives a molecular weight of 504, which is in good agreement with the calculated molecular weight (502.07) of the monomer **2a**. Interestingly, however, the average molecular weights ($M_{obsd}$) were observed to be concentration dependent: increasing the concentration of **2a** tended to gradually increase the average molecular weight and to approach twice the molecular weight of the monomer, which suggests formation of the dimer **3a** at higher concentrations. A plot of $M_{obsd}$ against the concentration of **2a** shows a downward curvature as depicted in Figure 2. The data obtained nicely fit the dissociation-association equilibrium model shown in Scheme 1, and dissociation and association constants of **2a** were calculated by least squares estimation according to eq. 1 to yield $K_{dissoc} = 2.66\times10^{-5}$ M and $K_{assoc} = 2.6\times10^{2}$ $M^{-1}$, respectively [4].

$$M_{obsd} = M_{2a}(1 + [\mathbf{1a}]/K_{dissoc} + 2K_{assoc}[\mathbf{1a}]^3/K_{dissoc}^2)/ (2 + [\mathbf{1a}]/K_{dissoc} + K_{assoc}[\mathbf{1a}]^3/K_{dissoc}^2) \quad (1)$$

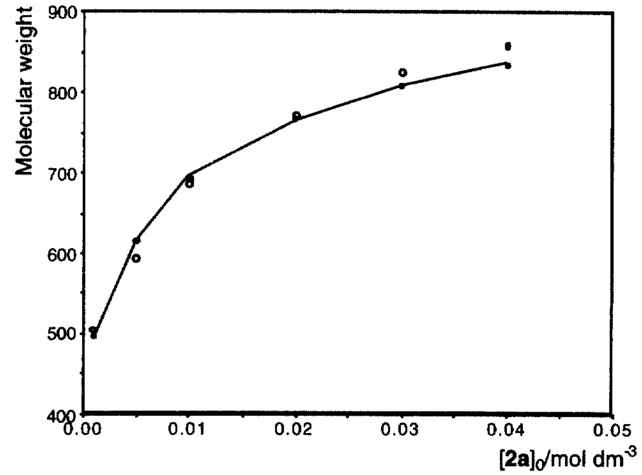


**Figure 2.** Molecular weights of $\lambda^3$-bromoiodane **2a** in chloroform solution measured by vapor pressure osmometry at 25 °C (○). Calculated molecular weights (●).

Here, $M_{2a}$ is the calculated molecular weight of the monomer **2a**. The value of $K_{dissoc}$ of **2a** obtained is comparable to that reported for *(E)-t*-BuCH=CHI(Ph)Cl under more polar conditions (in chloroform at $\mu = 0.1$), as mentioned above. The β-bromo substituent in **2a** has been shown to decrease the dissociation constant, probably by stabilizing the hypervalent bonding as a more electronegative apical ligand [5].

Further evidence for the dissociation and association equilibria of $\lambda^3$-iodane **2a** in chloroform solution shown in Scheme 1 comes from $^1$H NMR measurements. Chemical shifts of the vinylic and aromatic protons of $\lambda^3$-vinylbromoiodane **2a** in $CDCl_3$ at 25 °C are concentration dependent (Figure 3). The resonances of the vinylic proton move increasingly downfield with increasing concentration of **2a**, while the signals of the *meta* and *para* protons shift upfield. The chemical shift data can be simulated by a nonlinear least-squares method according to eq. 2 by using the equilibrium constants determined by vapor pressure osmometry and the parameters given in Table 1 [6].

$$\delta_{obsd} = (\delta_1 + \delta_2\,[\mathbf{1a}]/K_{dissoc} + 2\delta_3 K_{assoc}[\mathbf{1a}]^3/K_{dissoc}{}^2)/$$
$$(1 + [\mathbf{1a}]/K_{dissoc} + 2K_{assoc}[\mathbf{1a}]^3/K_{dissoc}{}^2) \qquad (2)$$

Here, $\delta_1$, $\delta_2$, and $\delta_3$ are the $^1$H NMR chemical shifts of ion **1a**, monomer **2a**, and dimer **3a**, respectively. The solid lines in Figures 3 show the fits of the observed chemical shifts to eq 2. The downfield shift ($\delta$ 8.39 ppm) of the vinylic proton in the iodonium ion **1a** compared to that ($\delta$ 6.61 ppm) in **2a** is in line with the observed chemical shift: $^1$H NMR measurement of $\lambda^3$-vinylbromoiodane **2a** in acetone-$d_6$ and DMSO-$d_6$ ($4\times10^{-3}$ M) showed the resonance of the vinylic proton at $\delta$ 7.82 and 8.10 ppm, respectively. Since cryoscopic measurement of diphenyliodonium bromide indicates complete dissociation in DMSO [1d], it seems reasonable to assume that the bromoiodane **2a** will be highly dissociated into the iodonium ion **1a** in DMSO. An NOE enhancement observed between the vinylic and *ortho* protons in $CDCl_3$ at $1\times10^{-1}$ M might be compatible with formation of the dimer **3a**.

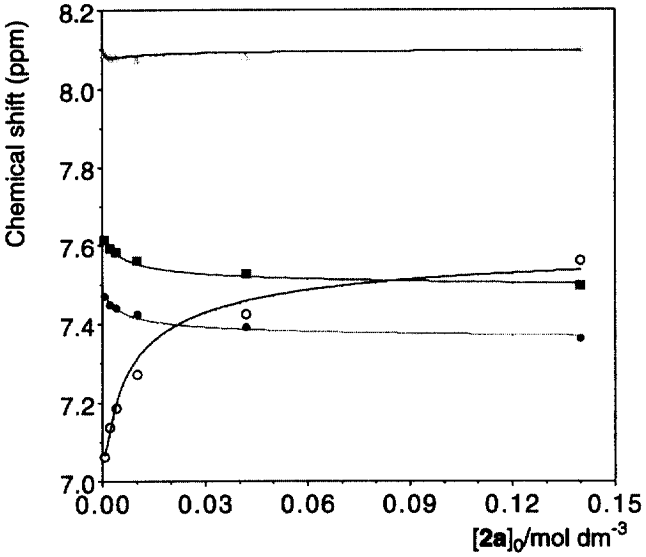


**Figure 3.** Change in $^1$H NMR chemical shift of $\lambda^3$-bromoiodane **2a** measured in $CDCl_3$ at 25 °C: (○) vinylic H; (▲) *ortho* H; (●) *meta* H; (■) *para* H. The solid curve is calculated.

**Table 1** Chemical Shift Parameters (ppm) Used for the Curve Fittings in Figure 3

| | vinylic H | *ortho* H | *meta* H | *para* H |
|---|---|---|---|---|
| ion **1a** | 8.39 | 8.36 | 7.26 | 7.39 |
| monomer **2a** | 6.61 | 8.02 | 7.55 | 7.70 |
| dimer **3a** | 7.65 | 8.10 | 7.35 | 7.48 |

In the solid state of $\lambda^3$-haloiodanes, halogen-bridged dimeric structures similar to **3** were reported: for instance, three diphenylhaloiodanes ($Ar_2IX$: X = Cl, Br, I) are isomorphous centrosymmetic dimers, held together by halogen bridges [7].

To gain some understanding of the reaction of $\lambda^3$-iodanes it is important to determine the solution structures, because it is to be expected that free iodonium ions will be more reactive than hypervalent $\lambda^3$-iodanes which, in turn, are more reactive than iodane dimers.

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