

Evidence for  $\beta$ -Chlorocarbenium and  
 $\beta$ -Bromocarbenium Ions

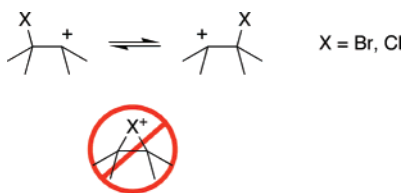
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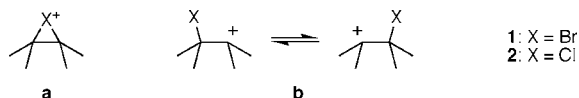
## ABSTRACT



Isotopic perturbation of degenerate equilibrium is used to determine whether tetramethylethylenchloronium and tetramethylethylenbromonium ions are closed 1,2-bridged structures or rapid equilibria of open  $\beta$ -halocarbenium ions. The observed  $^{13}\text{C}$  NMR isotope shifts are consistent with a combination of large equilibrium shifts and small upfield intrinsic shifts. The presence of equilibrium shifts in both halonium ions indicates that these ions are not closed 1,2-bridged structures. Rather, they are best represented by equilibria of  $\beta$ -halocarbenium ions.

A fundamental question in the study of 1,2-bridged halonium ions is whether they exist as closed structures with equal C–X bond orders (**a**) or as rapid equilibria of open  $\beta$ -halocarbenium structures with unequal bond orders (**b**).<sup>1</sup>

**Scheme 1.** Closed Halonium Ion (**a**) and Open  $\beta$ -Halocarbenium Ions (**b**)



On the basis of chemical shifts and carbon–fluorine coupling constants, Olah et al. showed that the tetramethylethylenefluoronium ion is an open  $\beta$ -fluorocarbenium ion.<sup>2</sup> A similar conclusion for the analogous bromonium (**1**) and chloronium (**2**) ions could not be made on the basis of chemical shifts.<sup>3</sup> A direct method for resolving these

structures is isotopic perturbation of degenerate equilibrium.<sup>4</sup> Servis and Domenick applied the method to **1-d<sub>6</sub>** and concluded that the ion is a closed structure (**1a**).<sup>5</sup> We applied the method to **2-d<sub>3</sub>** and now report it is an equilibrium of  $\beta$ -chlorocarbenium ions (**2b**). Additionally, we provide evidence for 1,2-methyl shifts in both **1-d<sub>6</sub>** and **2-d<sub>3</sub>**. On the basis of this new evidence, we reexamined Servis' work and report **1-d<sub>6</sub>** is also an equilibrium of  $\beta$ -bromocarbenium ions (**1b**).

As its name suggests, isotopic perturbation of degenerate equilibrium uses equilibrium isotope effects to alter dynamically equivalent  $^{13}\text{C}$  NMR chemical shifts. The method requires molecules with an asymmetric distribution of deuteria. The observed  $^{13}\text{C}$  chemical shift difference between the labeled and nonlabeled molecules ( $\Delta_{\text{obs}} = \delta_{\text{C(D)}} - \delta_{\text{C(H)}}$ ) can indicate the presence of an equilibrium. In both closed and open structures, the deuteria impart intrinsic isotope shifts ( $^n\Delta_{\text{o}}$ , where  $n$  is the number of bonds between the carbon and deuterium). These shifts are typically small, upfield

(1) (a) Olah, G. A. *Halonium Ions*; Wiley-Interscience: New York, 1975; pp 113–116 and references therein. (b) Ruasse, M.-F. *Acc. Chem. Res.* **1990**, 23, 87. (c) Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Sebolcak-Tilk, H. *J. Am. Chem. Soc.* **1991**, 113, 8012.

(2) (a) Olah, G. A.; Bollinger, J. M. *J. Am. Chem. Soc.* **1967**, 89, 4744. (b) Olah, G. A.; Prakash, G. K. S.; Krishnamurthy, V. V. *J. Org. Chem.* **1983**, 48, 5516.

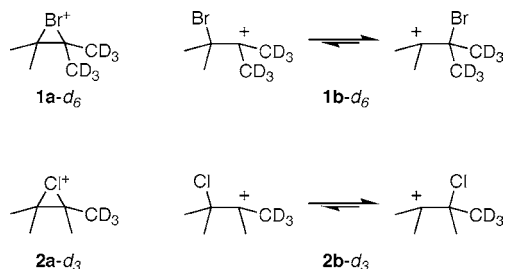
(3) Olah, G. A.; Westerman, P. W.; Melby, E. G.; Mo, Y. K. *J. Am. Chem. Soc.* **1974**, 96, 3565.

(4) (a) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, 99, 8070. (b) Siehl, H.-U. *Adv. Phys. Org. Chem.* **1987**, 23, 63. (c) Forsyth, D. A. *Isotopes in Organic Chemistry*; Buncl, E., Lee, C. C., Eds; Elsevier: Amsterdam, The Netherlands, 1987; Vol. 6, Chapter 1. (d) Perrin, C. L.; Ohta, B. K. *Bioorg. Chem.* **2002**, 30, 3.

(5) Servis, K. L.; Domenick, R. L. *J. Am. Chem. Soc.* **1985**, 107, 7186.

(negative), and attenuate as  $n$  increases.<sup>4c,6</sup> If the ions are closed (**1a-d<sub>6</sub>** and **2a-d<sub>3</sub>** in Scheme 2), intrinsic isotope shifts

**Scheme 2.** Closed and Open Structure for **1-d<sub>6</sub>** and **2-d<sub>3</sub>**

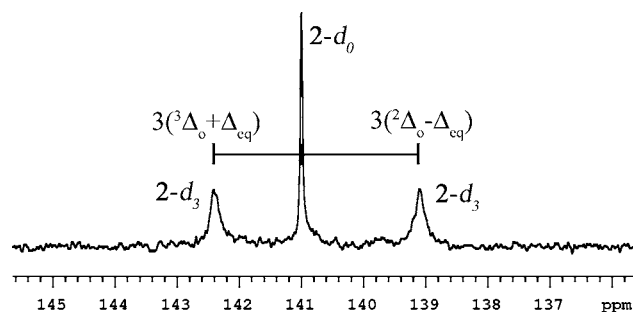


on the quaternary carbons are expected to be small upfield  ${}^2\Delta_o$  and  ${}^3\Delta_o$ .

However if the ions are equilibria of open  $\beta$ -halocarbenium ions (**1b-d<sub>6</sub>** and **2b-d<sub>3</sub>**), the deuteria impart an equilibrium isotope shift ( $\Delta_{eq}$ ) in addition to  $\Delta_o$ . The  $\Delta_{eq}$  arises from  $\beta$ -deuterium isotope effects on the carbenium center, a destabilizing effect that causes the equilibrium to favor the isotopomer with deuteria distal to the carbenium center.<sup>7</sup> Thus, the time averaged  ${}^{13}\text{C}$  NMR signal for the quaternary carbon distal to the deuteria should appear downfield while the proximal carbon signal should appear upfield. The key feature of equilibrating systems is the appearance of a large  $\Delta_{eq}$  in which symmetrically related carbon signals are displaced by equal magnitudes and in opposite directions.

In summary, isotopic perturbation of degenerate equilibrium predicts that the  ${}^{13}\text{C}$  NMR spectrum of halonium ions will be qualitatively different from an equilibrium mixture of  $\beta$ -halocarbenium ions. For example, the quaternary carbons of **2a-d<sub>3</sub>** should exhibit small upfield (negative)  $\Delta_o$  relative to **2a-d<sub>0</sub>**, the nonlabeled chemical shift reference:  $\Delta_{obs} = 3({}^3\Delta_o)$  and  $\Delta_{obs} = 3({}^2\Delta_o)$ . For **2b-d<sub>3</sub>**, the  $\Delta_{eq}$  will dominate and the carbon proximal to the deuteria will appear far upfield of **2b-d<sub>0</sub>**:  $\Delta_{obs} = 3({}^2\Delta_o - \Delta_{eq})$ . The signal of the carbon distal to the deuteria will appear far downfield of **2b-d<sub>0</sub>**:  $\Delta_{obs} = 3({}^3\Delta_o + \Delta_{eq})$ . Thus, the presence of the large upfield and downfield shifts for the quaternary carbons of **2-d<sub>3</sub>** indicates the presence of  $\Delta_{eq}$  and supports open  $\beta$ -chlorocarbenium ions.

The deuterated precursors to halonium ions **1** and **2** were prepared by known procedures.<sup>8</sup> The deuterium content was >95% by NMR. Halonium ions were prepared under stable ion conditions ( $\text{SbF}_5/\text{SO}_2$  at  $-60^\circ\text{C}$ ).<sup>2a</sup> Spectra of **1-d<sub>6</sub>**, **2-d<sub>3</sub>**, **2-d<sub>0</sub>**, and a 2:1 mixture of **2-d<sub>3</sub>** to **2-d<sub>0</sub>** were obtained on a Varian Mercury 300 NMR spectrometer (75 MHz  ${}^{13}\text{C}$ ) fitted



**Figure 1.** The quaternary carbon region of the  ${}^{13}\text{C}$  NMR spectrum of a 2:1 mixture of **2-d<sub>3</sub>** and **2-d<sub>0</sub>** at  $-60^\circ\text{C}$ .

with a 10 mm probe. The samples were prepared in NMR tube inserts (Wilmad) and acetone- $d_6$  was placed in the outer tube to act as both a lock solvent and chemical shift reference (29.8 ppm).

Figure 1 shows the quaternary carbon region of the  ${}^{13}\text{C}$  spectrum for a 2:1 mixture of **2-d<sub>3</sub>** and **2-d<sub>0</sub>**. There are two signals for **2-d<sub>3</sub>** separated by 3.32 ppm. The lone signal for **2-d<sub>0</sub>** resides between the **2-d<sub>3</sub>** peaks and acts as an internal reference to calculate  $\Delta_{obs}$ . For the quaternary carbons of **2-d<sub>3</sub>**, the  $\Delta_{obs}$  are +1.42 and  $-1.90$  ppm.

The two  $\Delta_{obs}$  values of **2-d<sub>3</sub>** can be understood in the framework of an isotopic perturbation of an equilibrium involving open  $\beta$ -chlorocarbenium ions. The shifts are consistent with small downfield intrinsic shifts in combination with large equilibrium shifts that move the signals away from the **2-d<sub>0</sub>** signal. The downfield  $\Delta_{obs}$  corresponds to the quaternary carbon distal to the deuteria and is shifted by  $3({}^3\Delta_o + \Delta_{eq}) = +1.42$  ppm. The upfield  $\Delta_{obs}$  corresponds to the carbon proximal to the deuteria and is shifted by  $3({}^2\Delta_o - \Delta_{eq}) = -1.90$  ppm. The absolute values of  ${}^2\Delta_o$ ,  ${}^3\Delta_o$ , and  $\Delta_{eq}$  cannot be calculated from the data; however, the sum  $3({}^2\Delta_o + {}^3\Delta_o) = -0.48$  ppm is consistent with typical two- and three-bond intrinsic shifts.<sup>4c,6</sup>

The  $\Delta_{obs}$  do not change between  $-60$  and  $-80^\circ\text{C}$ . Although others have pointed out that the absence of a temperature dependence of  $\Delta_{obs}$  is inconsistent with the proposal of an equilibrium,<sup>5,9</sup> it is possible that the dependence is small and could go undetected in the observed temperature range. In the solvolysis of isopropyl- $d_6$  halides and sulfonates, Leffek et al. observed a  $\beta$ -secondary deuterium isotope effect that did not change over a  $30^\circ\text{C}$  temperature range.<sup>10</sup> Assuming the equilibrium isotope effect is due to the enthalpic contribution to the free energy, a lower bound of  $\Delta H$  for the temperature-dependent regime can be determined. On the basis of estimates of chemical shifts in **2b** and the limit of detection for shift changes in the NMR, the lower bound on the absolute value of  $\Delta H$  is estimated to be 6.7 cal/mol.<sup>11</sup>

(6) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 106.

(7) DeFrees, D. J.; Taagepera, M.; Levi, B. A.; Pollack, S. K.; Summerhays, K. D.; Taft, R. W.; Wolfsberg, M.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5532.

(8) Deuterium was incorporated into the precursor of **1-d<sub>6</sub>** by treating acetone- $d_6$  with isopropylmagnesium bromide. Subsequent dehydration and bromine addition yielded the appropriately labeled precursor. Deuterium was incorporated into the precursor of **2-d<sub>3</sub>** by base-catalyzed exchange of pinacolone in  $\text{D}_2\text{O}/\text{MeOD}$ . Treatment of pinacolone- $d_3$  with  $\text{PCl}_5$  yielded the appropriately labeled precursor.

(9) Forsyth, D. A.; Botkin, J. H.; Puckace, J. S.; Servis, K. L.; Domenick, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 7270.

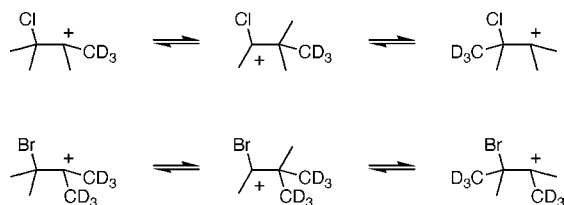
(10) Leffek, K. T.; Robertson, R. E.; Sugamori, S. E. *Can. J. Chem.* **1961**, *39*, 1989.

Preliminary attempts to estimate  $\Delta H$  by calculating the ZPE's of each isotopomer of **2b-d<sub>3</sub>** indicate that these calculations are not trivial. In vacuo, geometry optimization of an initially open structure yields a closed halonium ion. Because a stationary point that represents an open structure is a requirement for the frequency calculations, a discrete solvent model was used to obtain an optimized structure for **2b**. With the introduction of a single SO<sub>2</sub> molecule, geometry optimization of the **2b**-SO<sub>2</sub> complex at the MP2/6-31G\* level generates stationary points corresponding to open structures. However, the frequency calculations are sensitive to the solvent configuration in the **2b**-SO<sub>2</sub> complex. Our initial estimates indicate that the calculation method is not precise enough to determine whether  $\Delta H$  is below the lower bound; the estimated range of  $\Delta H$  is  $-9.6$  to  $28.7$  cal/mol.

The <sup>13</sup>C NMR spectra of **2-d<sub>3</sub>** taken between  $-60$  and  $-80$  °C indicate an interesting dynamic behavior. The line shapes of the quaternary signals sharpen at low temperature. This result indicates that the methyl-d<sub>3</sub> group migrates between quaternary carbons on the NMR time scale. The methyl signals show similar behavior but because the chemical shift difference between interchanging methyl groups is smaller, the full coalescence behavior can be observed within the temperature range. At  $-80$  °C, two methyl signals appear and result from different intrinsic shifts for the methyl-d<sub>0</sub> groups that are geminal (<sup>3</sup>Δ<sub>o</sub>) or vicinal (<sup>4</sup>Δ<sub>o</sub>) to the methyl-d<sub>3</sub> group. At  $-60$  °C, a single signal appears in the spectrum.

A likely mechanism that explains these data consists of a series of 1,2-methyl shifts (Scheme 3). Similar 1,2-methyl

**Scheme 3.** Methyl Shifts in **1-d<sub>6</sub>** and **2-d<sub>3</sub>**

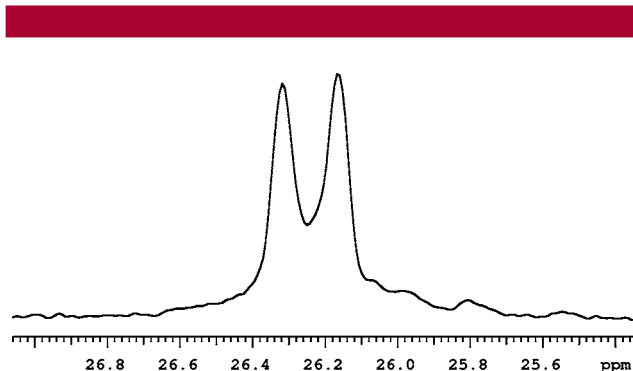


shifts were observed by Olah et al. in the isomerization of 2-butenonium ion at  $-40$  °C<sup>12</sup> and as a proposed mechanism for equilibrating  $\beta$ -fluorocarbenium ions.<sup>2b</sup> The 1,2-methyl shifts do not affect the analysis of the equilibrium of  $\beta$ -chlorocarbenium ions because the  $\Delta_{eq}$  appears at low temperatures when the methyl migration is slow. Additionally, methyl-d<sub>3</sub> shifts in **2-d<sub>3</sub>** generate identical asymmetrically labeled isotopomers.

Considering our evidence for  $\beta$ -chlorocarbenium ions and the presence of 1,2-methyl shifts, we reexamined the work of Servis and Domenick to determine whether methyl shifts

(11) The equilibrium isotope shift of **2b-d<sub>3</sub>** can be calculated from equations found in ref 4b. Chemical shifts of **2b** were calculated by using B3LYP/6-311G\* GIAO calculations of the **2b**-SO<sub>2</sub> complex (vide infra). The limit of detection for the difference in the observed isotope shifts was estimated to be 0.1 ppm.

(12) Olah, G. A.; Bollinger, J. M.; Brinich, J. M. *J Am. Chem. Soc.* **1968**, *90*, 2587.



**Figure 2.** The methyl carbon region of the <sup>13</sup>C NMR spectrum of **1-d<sub>6</sub>** at  $-60$  °C.

occur in **1-d<sub>6</sub>**. As mentioned above, methyl shifts in **2-d<sub>3</sub>** generate identical isotopomers and, in the slow exchange regime, will not affect the analysis of isotope shifts. This is not the case for **1-d<sub>6</sub>**. Methyl shifts will generate a mixture of isotopomers with geminal and vicinal orientations of the methyl-d<sub>3</sub> groups (Scheme 3). Additionally, the symmetric displacement of deuteria for the isotopomer with vicinal methyl-d<sub>3</sub> groups causes the equilibrium to be degenerate and therefore these isotopomers will exhibit  $\Delta_o$  only.

Figure 2 shows the methyl carbon region of the <sup>13</sup>C NMR spectrum of **1-d<sub>6</sub>**. The presence of two signals is inconsistent with a single isotopomer containing geminal methyl-d<sub>3</sub> groups. Rather, the data are consistent with a mixture of isotopomers with vicinal and geminal methyl-d<sub>3</sub> groups. Thus, 1,2-methyl shifts occur in **1** and the sample of **1-d<sub>6</sub>** should be considered a mixture when analyzing the quaternary carbon region of the <sup>13</sup>C NMR.

The quaternary carbon region of the NMR spectrum of **1-d<sub>6</sub>** is qualitatively similar to Figure 1 but with the central signal nearly equidistant from the outer signals.<sup>13</sup> The  $\Delta_{obs}$  of the two downfield signals are consistent with those previously reported by Servis,  $+1.50$  and  $-0.30$  ppm.<sup>5</sup> The additional signal appears upfield of the others ( $\Delta_{obs} = -2.11$  ppm).

These signals can be understood in the framework of an isotopic perturbation of equilibrium on a mixture of isotopomers. The central signal is assigned to isotopomers with vicinal methyl-d<sub>3</sub> groups which show  $\Delta_o$  only. The  $\Delta_{obs}$  for both quaternary carbons of this isotopomer are identical:  $3(^2\Delta_o + ^3\Delta_o) = -0.30$  ppm. This sum is consistent with typical two- and three-bond intrinsic shifts. The outer signals are assigned to the geminal methyl-d<sub>3</sub> isotopomer and are consistent with a combination of intrinsic and equilibrium isotope shifts:  $6(^2\Delta_o - \Delta_{eq}) = -2.11$  ppm and  $6(^3\Delta_o + \Delta_{eq}) = +1.50$  ppm. The sum of intrinsic shifts,  $6(^2\Delta_o + ^3\Delta_o) = -0.61$  ppm, agrees with the value determined from the vicinal methyl-d<sub>3</sub> isotopomer.

(13) Additional signals appear in the spectrum which result from the loss of deuterium label. These signals can also be understood in the framework of 1,2-methyl shifts and isotopic perturbation of equilibrium of **1-d<sub>5</sub>**, **-d<sub>4</sub>**, **-d<sub>3</sub>**, **-d<sub>2</sub>**, and **-d<sub>1</sub>**. A signal for the nonlabeled isotopolog **1-d<sub>0</sub>** is also present and was used as the internal chemical shift reference.

The presence of  $\Delta_{\text{eq}}$  in **2**- $d_3$  and **1**- $d_6$  is consistent with the proposal that these ions are best described as equilibria of  $\beta$ -halocarbenium ions. To our knowledge, this is the first direct evidence to support  $\beta$ -chlorocarbenium and  $\beta$ -bromocarbenium ions as low-energy intermediates on the potential energy surface. These results contradict the generally accepted notion that closed chloronium and bromonium ion structures are solely responsible for stereospecific halogen addition to alkenes. The presence of equilibrium shifts does not rule out the existence of halonium ions. However, they do indicate that  $\beta$ -halocarbenium ions represent a significant contribution to the overall structure and, if present, halonium ions are in equilibrium with  $\beta$ -halocarbenium ions. Future experimental and theoretical investigations will determine if our conclusions are general and a more detailed report on these and other halonium ions is being prepared.

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**Supporting Information Available:** NMR spectra of **2**- $d_3$  at  $-50$  to  $-80$  °C and the quaternary carbon region of **1**- $d_6$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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