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Evidence for β-Chlorocarbenium and β-Bromocarbenium Ions

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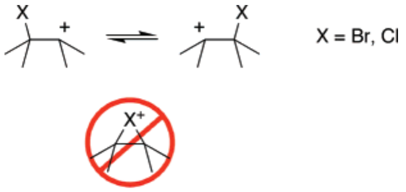
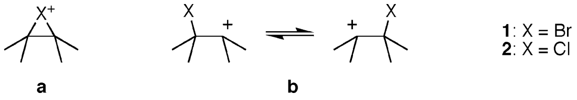
ABSTRACT



Isotopic perturbation of degenerate equilibrium is used to determine whether tetramethylethylenechloronium and tetramethylethylenebromonium ions are closed 1,2-bridged structures or rapid equilibria of open β-halocarbenium ions. The observed ^{13}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 β-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 β-halocarbenium structures with unequal bond orders (**b**).[1]

Scheme 1. Closed Halonium Ion (**a**) and Open β-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 β-fluorocarbenium ion.[2] A similar conclusion for the analogous bromonium (**1**) and chloronium (**2**) ions could not be made on the basis of chemical shifts.[3] A direct method for resolving these structures is isotopic perturbation of degenerate equilibrium.[4] Servis and Domenick applied the method to **1**-d_6 and concluded that the ion is a closed structure (**1a**).[5] We applied the method to **2**-d_3 and now report it is an equilibrium of β-chlorocarbenium ions (**2b**). Additionally, we provide evidence for 1,2-methyl shifts in both **1**-d_6 and **2**-d_3. On the basis of this new evidence, we reexamined Servis' work and report **1**-d_6 is also an equilibrium of β-bromocarbenium ions (**1b**).

As its name suggests, isotopic perturbation of degenerate equilibrium uses equilibrium isotope effects to alter dynamically equivalent ^{13}C NMR chemical shifts. The method requires molecules with an asymmetric distribution of deuteria. The observed ^{13}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 ($^n\Delta_o$, where n is the number of bonds between the carbon and deuterium). These shifts are typically small, upfield

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(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.; Slebolcak-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*; Buncel, 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.

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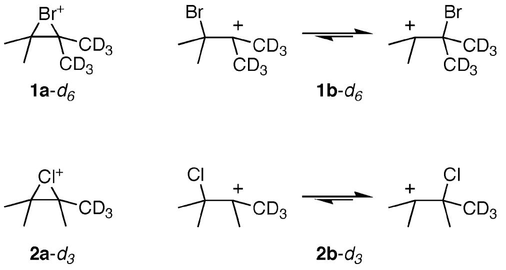
(negative), and attenuate as n increases.[4c,6] If the ions are closed (**1a**-d_6 and **2a**-d_3 in Scheme 2), intrinsic isotope shifts on the quaternary carbons are expected to be small upfield $^2\Delta_o$ and $^3\Delta_o$.

Scheme 2. Closed and Open Structure for **1**-d_6 and **2**-d_3



However if the ions are equilibria of open β-halocarbenium ions (**1b**-d_6 and **2b**-d_3), the deuteria impart an equilibrium isotope shift (Δ_{eq}) in addition to Δ_o. The Δ_{eq} arises from β-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.[7] Thus, the time averaged ^{13}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 Δ_{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}C NMR spectrum of halonium ions will be qualitatively different from an equilibrium mixture of β-halocarbenium ions. For example, the quaternary carbons of **2a**-d_3 should exhibit small upfield (negative) Δ_o relative to **2a**-d_0, the nonlabeled chemical shift reference: $\Delta_{obs} = 3(^3\Delta_o)$ and $\Delta_{obs} = 3(^2\Delta_o)$. For **2b**-$d_3$, the Δ_{eq} will dominate and the carbon proximal to the deuteria will appear far upfield of **2b**-d_0: $\Delta_{obs} = 3(^2\Delta_o - \Delta_{eq})$. The signal of the carbon distal to the deuteria will appear far downfield of **2b**-d_0: $\Delta_{obs} = 3(^3\Delta_o + \Delta_{eq})$. Thus, the presence of the large upfield and downfield shifts for the quaternary carbons of **2**-d_3 indicates the presence of Δ_{eq} and supports open β-chlorocarbenium ions.

The deuterated precursors to halonium ions **1** and **2** were prepared by known procedures.[8] The deuterium content was >95% by NMR. Halonium ions were prepared under stable ion conditions (SbF_5/SO_2 at −60 °C).[2a] Spectra of **1**-d_6, **2**-d_3, **2**-d_0, and a 2:1 mixture of **2**-d_3 to **2**-d_0 were obtained on a Varian Mercury 300 NMR spectrometer (75 MHz ^{13}C) fitted 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).

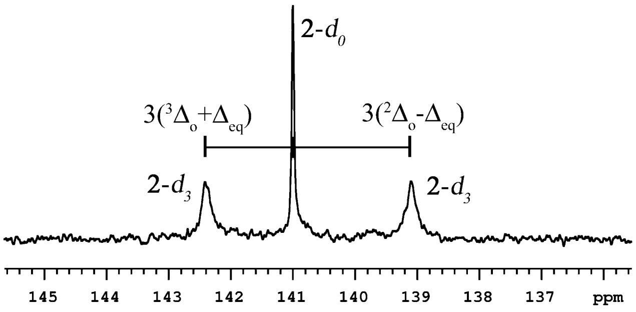


Figure 1. The quaternary carbon region of the ^{13}C NMR spectrum of a 2:1 mixture of **2**-d_3 and **2**-d_0 at −60 °C.

Figure 1 shows the quaternary carbon region of the ^{13}C spectrum for a 2:1 mixture of **2**-d_3 and **2**-d_0. There are two signals for **2**-d_3 separated by 3.32 ppm. The lone signal for **2**-d_0 resides between the **2**-d_3 peaks and acts as an internal reference to calculate Δ_{obs}. For the quaternary carbons of **2**-d_3, the Δ_{obs} are +1.42 and −1.90 ppm.

The two Δ_{obs} values of **2**-d_3 can be understood in the framework of an isotopic perturbation of an equilibrium involving open β-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_0 signal. The downfield Δ_{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 Δ_{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 Δ_{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.[4c,6]

The Δ_{obs} do not change between −60 and −80 °C. Although others have pointed out that the absence of a temperature dependence of Δ_{obs} is inconsistent with the proposal of an equilibrium,[5,9] 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 β-secondary dueterium isotope effect that did not change over a 30 °C temperature range.[10] Assuming the equilibrium isotope effect is due to the enthalpic contribution to the free energy, a lower bound of ΔH 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 ΔH is estimated to be 6.7 cal/mol.[11]

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[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_6 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_3 by base-catalyzed exchange of pinacolone in D_2O/MeOD. Treatment of pinacolone-d_3 with 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.

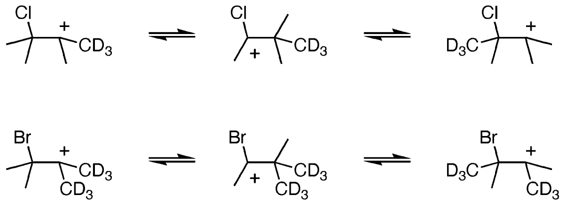
[10] Leffek, K. T.; Robertson, R. E.; Sugamori, S. E. *Can. J. Chem.* **1961**, *39*, 1989.

Preliminary attempts to estimate ΔH by calculating the ZPE's of each isotopomer of **2b**-d_3 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_2 molecule, geometry optimization of the **2b**-SO_2 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_2 complex. Our initial estimates indicate that the calculation method is not precise enough to determine whether ΔH is below the lower bound; the estimated range of ΔH is -9.6 to 28.7 cal/mol.

The ^{13}C NMR spectra of **2**-d_3 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_3 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_0 groups that are geminal ($^3\Delta_o$) or vicinal ($^4\Delta_o$) to the methyl-d_3 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 shifts were observed by Olah et al. in the isomerization of 2-butenebromonium ion at -40 °C[12] and as a proposed mechanism for equilibrating β-fluorocarbenium ions.[2b] The 1,2-methyl shifts do not affect the analysis of the equilibrium of β-chlorocarbenium ions because the Δ_{eq} appears at low temperatures when the methyl migration is slow. Additionally, methyl-d_3 shifts in **2**-d_3 generate identical asymmetrically labeled isotopomers.

Scheme 3. Methyl Shifts in **1**-d_6 and **2**-d_3



Considering our evidence for β-chlorocarbenium ions and the presence of 1,2-methyl shifts, we reexamined the work of Servis and Domenick to determine whether methyl shifts occur in **1**-d_6. As mentioned above, methyl shifts in **2**-d_3 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_6. Methyl shifts will generate a mixture of isotopomers with geminal and vicinal orientations of the methyl-d_3 groups (Scheme 3). Additionally, the symmetric displacement of deuteria for the isotopomer with vicinal methyl-d_3 groups causes the equilibrium to be degenerate and therefore these isotopomers will exhibit Δ_o only.

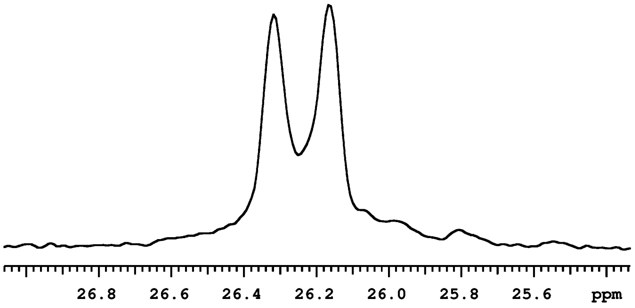


Figure 2. The methyl carbon region of the ^{13}C NMR spectrum of **1**-d_6 at -60 °C.

Figure 2 shows the methyl carbon region of the ^{13}C NMR spectrum of **1**-d_6. The presence of two signals is inconsistent with a single isotopomer containing geminal methyl-d_3 groups. Rather, the data are consistent with a mixture of isotopomers with vicinal and geminal methyl-d_3 groups. Thus, 1,2-methyl shifts occur in **1** and the sample of **1**-d_6 should be considered a mixture when analyzing the quaternary carbon region of the ^{13}C NMR.

The quaternary carbon region of the NMR spectrum of **1**-d_6 is qualitatively similar to Figure 1 but with the central signal nearly equidistant from the outer signals.[13] The Δ_{obs} of the two downfield signals are consistent with those previously reported by Servis, $+1.50$ and -0.30 ppm.[5] 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_3 groups which show Δ_o only. The Δ_{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_3 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_3 isotopomer.

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[11] The equilibrium isotope shift of **2b**-d_3 can be calculated from equations found in ref 4b. Chemicals shifts of **2b** were calculated by using B3LYP/6-311G* GIAO calculations of the **2b**-SO_2 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.

[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_5, -d_4, -d_3, -d_2, and -d_1. A signal for the nonlabeled isotopolog **1**-d_0 is also present and was used as the internal chemical shift reference.

The presence of Δ_{eq} in **2**-d_3 and **1**-d_6 is consistent with the proposal that these ions are best described as equilibria of β-halocarbenium ions. To our knowledge, this is the first direct evidence to support β-chlorocarbenium and β-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 existenece of halonium ions. However, they do indicate that β-halocarbenium ions represent a significant contribution to the overall structure and, if present, halonium ions are in equilibrium with β-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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