

## The structure of halonium ions in superacidic solutions\*

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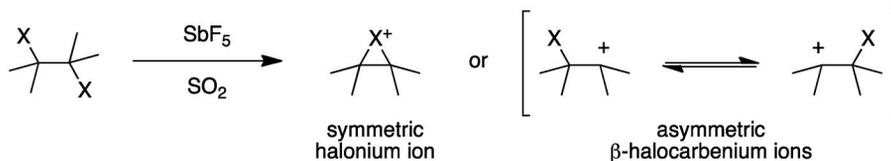
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**Abstract:** Isotopic perturbation of equilibrium was applied to 1,2-bridged halonium ions to determine whether they exist as single symmetric structures or as a rapid equilibrium of asymmetric structures. The observed deuterium isotope shifts are qualitatively and quantitatively consistent with the presence of intrinsic and equilibrium isotope shifts. The presence of equilibrium shifts suggests that these ions exist as a rapid equilibrium of asymmetric structures. Though the asymmetric structures were initially ascribed to  $\beta$ -halocarbenium ions, subsequent computational data suggest that 1,2-bridged halonium ions react with sulfur dioxide ( $\text{SO}_2$ ), the experimental solvent. Our current hypothesis is that the equilibrium isotope shifts result from rapid labile addition of  $\text{SO}_2$  to the halonium ions. Other hypotheses have been invoked to explain the results and are considered in the context of the available data.

**Keywords:** carbocations; chemical equilibrium; NMR; isotopes; reaction mechanisms.

### INTRODUCTION

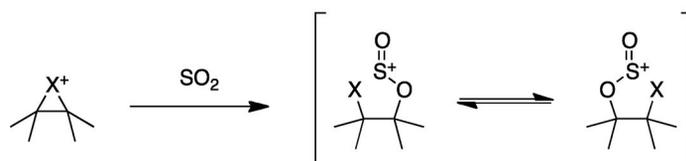
Bridged halonium ions are a general class of compounds characterized by a hypervalent, positively charged halogen atom that bridges two carbon atoms. A fundamental question in the study of bridged halonium ions is whether they exist as a single symmetric structure with equal carbon–halogen bond orders or as a rapidly equilibrating mixture involving asymmetric halocarbenium ions with unequal bond orders (Scheme 1) [1–3]. The question applied to carbonium ions, also known as nonclassical ions, was undisputedly controversial [4–7]. Surprisingly, the question applied to halonium ions received comparatively little scrutiny. Currently, the symmetric 1,2-bridged bromonium ions are depicted in introductory organic chemistry texts and are considered the canonical example of a symmetric halonium ion [8].



**Scheme 1** Symmetric halonium ions and equilibrium of asymmetric  $\beta$ -halocarbenium ions, generated under superacidic conditions.

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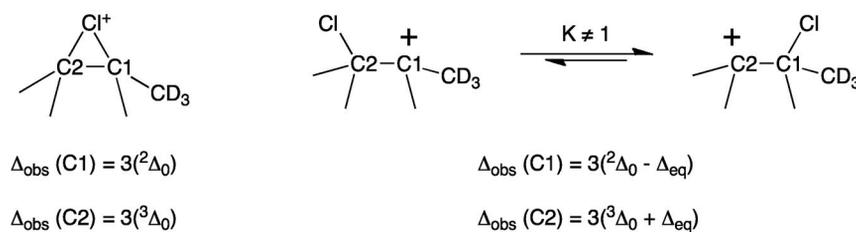
In the past few years, our laboratory has challenged the prevailing notion that 1,2-bridged halo-nium ions generated under superacidic conditions are symmetric. Initially, we proposed that these ions are rapid equilibria of  $\beta$ -halocarbenium ions [9]. On the basis of subsequent computational data, we altered our hypothesis and are now skeptical that these ions are properly assigned as hypervalent halo-nium ions or halocarbenium ions [10]. Herein, I summarize the experimental and computational evidence in support of an equilibrium of asymmetric ions caused by the nucleophilic addition of sulfur dioxide ( $\text{SO}_2$ ) to the electron-deficient ions generated under superacidic conditions (Scheme 2). I also reinterpret experimental evidence from Olah's original characterizations [11,12], which at the time were curious anomalies, but now can be reinterpreted as supporting evidence for the presence of equilibria. Finally, I compare alternative hypotheses that may be invoked to explain the data.



**Scheme 2** Equilibrium of asymmetric ion- $\text{SO}_2$  complexes.

## METHODOLOGY

Isotopic perturbation of equilibrium is an elegant method that directly addresses the structural question of whether a molecule exists as a single symmetric structure or a rapidly interconverting mixture of asymmetric structures [13,14]. The method was developed by Martin Saunders and, as its name suggests, uses equilibrium isotope effects to alter dynamically equivalent NMR chemical shifts. It is a general method that has been reviewed in the literature and has been applied to chemical systems in which symmetry is in doubt [15]; examples include molecules that rapidly interconvert asymmetric isomers via pericyclic reactions [16], bond rotations [17], and proton transfers [18]. In the following, I provide a brief description of the method using symmetric and asymmetric  $2\text{-}d_3$  as examples (Scheme 3). Though the reasoning and illustrations use  $\beta$ -chlorocarbenium ions as the asymmetric ions, the method is valid for any equilibrium involving asymmetric structures and is therefore applicable to an equilibrium involving ion- $\text{SO}_2$  complexes as mentioned in the introduction.



**Scheme 3** Observed isotope shifts ( $\Delta_{\text{obs}}$ ) for symmetric  $2\text{-}d_3$  and an equilibrium of asymmetric  $\beta$ -chlorocarbenium ions.

The method requires the synthesis and NMR characterization of molecules with an asymmetric distribution of isotopes. For  $2\text{-}d_3$ , the deuteria are used to perturb the equilibrium and  $^{13}\text{C}$  are used as NMR-active, reporter nuclei. The observed isotope shift ( $\Delta_{\text{obs}}$ ) is the  $^{13}\text{C}$  NMR chemical shift difference between the deuterated and nondeuterated molecules ( $\Delta_{\text{obs}} = \delta_{\text{D}} - \delta_{\text{H}}$ ). The  $\Delta_{\text{obs}}$  is also the sum of two independent shifts: the intrinsic isotope shift ( $\Delta_0$ ) and the equilibrium isotope shift ( $\Delta_{\text{eq}}$ ).

In both symmetric and equilibrating asymmetric structures, the deuteria impart intrinsic isotope shifts ( ${}^n\Delta_0$ ) on nearby  ${}^{13}\text{C}$  nuclei. These shifts are typically small, upfield and attenuate as the number of intervening bonds ( $n$ ) increase. One-bond ( ${}^1\Delta_0$ ) and two-bond ( ${}^2\Delta_0$ ) intrinsic shifts are typically upfield and small, approximately  $-0.30$  and  $-0.10$  ppm per deuterium, respectively. Three-bond intrinsic shifts are further attenuated and (4-bond) shifts are typically too small to observe. For symmetric  $2-d_3$ , the  $\Delta_{\text{obs}}$  will be comprised of only  $\Delta_0$ . Specifically, the expected  $\Delta_{\text{obs}}$  for the quaternary carbons proximal to the deuteria (C1) in the symmetric ion  $2-d_3$  is  $3({}^2\Delta_0)$ , or approximately  $-0.30$  ppm. The expected  $\Delta_{\text{obs}}$  for the quaternary carbons distal to the deuteria (C2) is  $3({}^3\Delta_0)$ , and is expected to be smaller in magnitude than  $3({}^2\Delta_0)$ .

In only the equilibrating asymmetric structures, the deuteria will impart  $\Delta_{\text{eq}}$  in addition to  $\Delta_0$ . The  $\Delta_{\text{eq}}$  arises from a  $\beta$ -deuterium isotope effect, a destabilizing effect that causes the equilibrium to favor the isotopomer with deuteria distal to the carbenium center. For a rapid equilibrium of asymmetric  $2-d_3$ , the time-averaged  ${}^{13}\text{C}$  NMR signals will be biased toward the more stable isotopomer and C2 will be displaced downfield while C1 will be displaced upfield by  $\Delta_{\text{eq}}$ . Accordingly, the expected  $\Delta_{\text{obs}}$  for C1 is  $3({}^2\Delta_0 + \Delta_{\text{eq}})$  and C2 is  $3({}^3\Delta_0 + \Delta_{\text{eq}})$ . Again, the critical feature of equilibrating systems is the appearance of large  $\Delta_{\text{eq}}$ , which will displace C1 and C2 by equal magnitudes and in opposite directions.

The  $\Delta_{\text{eq}}$  can be calculated with the following formula:

$$\Delta_{\text{eq}} = \frac{\Delta(K-1)}{2(K-1)}$$

The equation is comprised of parameters that can be calculated with current computational methods. The isotopically perturbed equilibrium constant ( $K$ ) can be obtained from the ab initio vibrational force constants of the asymmetric structure [19]. The chemical shift difference between symmetrically related carbons ( $\Delta$ ) can be calculated using GIAO methods or the equivalent [20]. To compute both parameters, obtaining an accurate optimized geometry for the asymmetric structure is crucial.

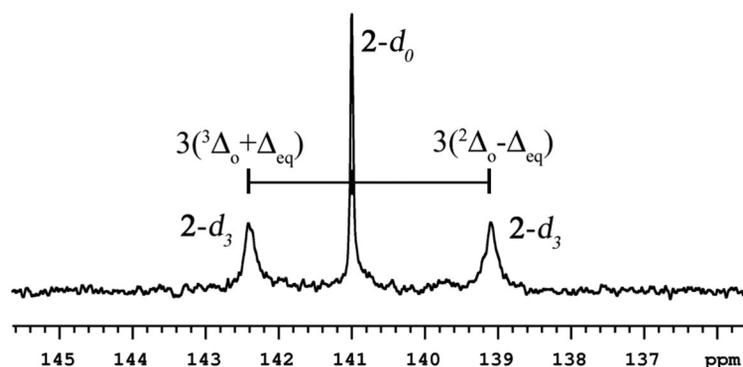
In summary, the question of symmetry can be determined by the qualitative and quantitative differences in the expected spectra for the symmetric structure and an equilibrium of asymmetric structures. In the symmetric structure, the observed isotope shifts are small and upfield relative to the non-labeled compound. Conversely, in an equilibrium of asymmetric structures, the observed isotope shifts are dominated by the equilibrium shift and are large and in opposing directions relative to the non labeled compound.

## TETRAMETHYLETHYLENE HALONIUM IONS

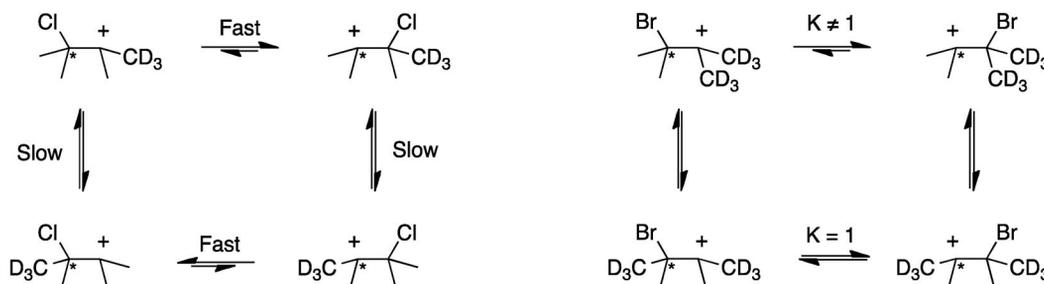
The  ${}^{13}\text{C}$  NMR spectra for  $1-d_6$  and  $2-d_3$  were obtained, and the  $\Delta_{\text{obs}}$  were referenced to an internal  $-d_0$  standard. The  $\Delta_{\text{obs}}$  for the quaternary carbons of  $1-d_6$  were  $+1.50$  and  $-2.11$  ppm. The  $\Delta_{\text{obs}}$  for the quaternary carbons of  $2-d_3$  were  $+1.42$  and  $-1.90$  ppm. The spectrum of  $2-d_3$  expanded about the quaternary carbons is presented in Fig. 1. Both sets of data are quantitatively and qualitatively consistent with the sum of small upfield intrinsic shifts and large opposing equilibrium shifts.

At  $-60$  °C, the  $2-d_3$  signals were significantly broadened relative to the  $2-d_0$  signal. The broadening was temperature dependent; raising the temperature to  $-50$  °C further broadened the signal into the baseline and lowering the temperature sharpened the signals. We attributed the broadening to a dynamic effect caused by 1,2-methyl shifts that occur near the NMR timescale (Scheme 4). At low temperatures, the 1,2-shifts are slow and fix the relative position of the methyl- $d_3$  group to the  ${}^{13}\text{C}$  reporter nuclei. At high temperatures, the 1,2-shifts are fast and the  ${}^{13}\text{C}$  signal becomes a time-averaged signal.

The spectrum for  $1-d_6$  in the absence of  $1-d_0$  was complex, consisting of 21 observable peaks. The complexity can be understood in the context of 1,2-methyl shifts and a process that exchanges deuterons for protons. The 1,2-methyl shifts are similar to those observed for  $2-d_3$ . But in this case, the rates are slow on the NMR timescale but large enough to scramble the relative positions of the two



**Fig. 1**  $^{13}\text{C}$  NMR spectrum of a 1:1 mixture of  $2\text{-}d_3$  and  $2\text{-}d_0$  expanded about the quaternary carbon. Reprinted with permission from ref. [9]. Copyright 2007 American Chemical Society.



**Scheme 4** Isomerizations via 1,2-methyl shifts in  $2\text{-}d_3$  and  $1\text{-}d_6$ . A carbon is labeled as a reference.

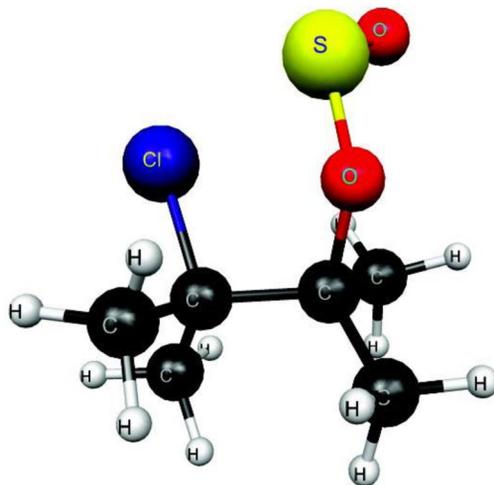
methyl- $d_3$  groups. Thus,  $1\text{-}d_6$  starts with geminally related methyl- $d_3$  groups but by the time of analysis, the methyl- $d_3$  groups scramble via 1,2-shifts to a statistical distribution of geminally and vicinally related methyl- $d_3$  groups. A second process exchanges deuterons for protons and yields a mixture of isotopologs with decreasing numbers of deuteria:  $1\text{-}d_6$ ,  $-d_5$ ,  $-d_4$ ,  $-d_3$ ,  $-d_2$ ,  $-d_1$ , and  $-d_0$ . In the context of these two processes, all 21 peaks can be assigned. Fortuitously, the  $-d_0$  isotopolog that was generated in situ was used as the internal reference and the  $\Delta_{\text{obs}}$  could be determined and are consistent with the  $\Delta_0$  when the molecule has a symmetric distribution of isotopes and  $\Delta_0 + \Delta_{\text{eq}}$  when the molecule has an asymmetric distribution.

In the decades since the introduction of isotopic perturbation of equilibrium, the presence of  $\Delta_{\text{obs}}$  that are consistent with  $\Delta_{\text{eq}}$  has become an established standard to conclude the existence of a rapid equilibrium involving asymmetric structures. However, Bogle and Singleton and have recently challenged this standard [21]. Using semi-classical Newtonian dynamics calculations to determine the vibrational averaged structure, they estimate the averaged nuclear positions and chemical shifts of  $1\text{-}d_6$ . Their calculations yield large isotope shift difference between quaternary carbons, a result consistent with the experimental observations described above. They attribute the shift difference coupling of anharmonic vibrational modes coupled to isotope-dependent vibrations. Thereby, they affirm the prevailing view that these ions are symmetric, but present a serious challenge to interpreting results from isotopic perturbation of equilibrium.

## COMPUTATIONAL EVIDENCE OF SO<sub>2</sub> NUCLEOPHILICITY

The initial goal of our computational studies was to calculate the equilibrium isotope shifts as described by Saunders [19]. However, obtaining a geometrically optimized asymmetrically bridged halonium ion proved difficult. In the search for minimized geometries, asymmetrically bridged halonium ions converged to symmetric halonium ions or  $\alpha$ -halocarbenium ions, the product after a 1,2-methyl shift. Using the transition state determined for breaking the C–X bond, we were able to perform intrinsic reaction coordinate calculations and found a shallow, high-energy minimum corresponding to the  $\beta$ -halocarbenium ion. The C–X bond was in the plane of the carbenium center, so there was no bridging between the halogen and carbenium carbon. The energy of this structure was approximately 15 kcal/mol higher in energy than the corresponding symmetric halonium ion, an energy difference that would attenuate  $\Delta_{\text{eq}}$  to an undetectable quantity.

Perrin has suggested that, when explicit solvent molecules are considered, the preponderance of asymmetric microstates can induce asymmetry in otherwise symmetric systems [22]. In other words, the equilibrium arises from interconversion of solvatomers, isomers that differ by solvation. In a crude attempt to model the asymmetry imposed by the solvent, a single molecule of SO<sub>2</sub>, the experimental solvent, was added in the calculation of a symmetric halonium ion [10]. But rather than produce an asymmetrically bridged halonium ion, the optimized structure exhibited geometric changes that suggested nucleophilic addition of the SO<sub>2</sub> to the halonium ion (Fig. 2). Notable structural features include a short C–O bond distance (1.6 Å), pyramidal quaternary carbons, a differential in the S–O bond distances, etc. The total energy of the system was lowered by the addition of SO<sub>2</sub> and was more than if the molecule were stabilizing the ion with its molecular dipole.



**Fig. 2** Optimized structure of the ion-SO<sub>2</sub> complex from **2** and SO<sub>2</sub>. Reprinted with permission from ref. [10]. Copyright 2008 American Chemical Society.

In the context of nucleophilic addition of SO<sub>2</sub> to halonium ions, the equilibrium, which was previously reported to involve asymmetrically bridged halonium ions or  $\beta$ -halocarbenium ions, can be now explained by labile addition of SO<sub>2</sub> to produce equilibrating asymmetric ion-SO<sub>2</sub> complexes. This surprising conclusion presents another difficult problem. The ion-SO<sub>2</sub> complexes are not halonium ions, asymmetrically bridged halonium ions, nor halocarbenium ions. Because all previously reported 1,2-bridged halonium ions were reported in the presence of SO<sub>2</sub>, the structural assignments of 1,2-bridged halonium ions are suspect.

## OTHER EVIDENCE IN SUPPORT OF ASYMMETRIC IONS

In the original characterizations of 1,2-bridged halonium ions, several curious anomalies were reported that, in the context of recent data, can be reinterpreted [11,12]. For example, in an attempt to characterize ethylene chloronium ion in  $\text{SbF}_5/\text{SO}_2$ , Olah et al. reported that, rather than a single signal consistent with the desired product, two triplets appeared in the  $^1\text{H}$  NMR. Additionally, though they observed a single signal for the ethylene bromonium ion in  $\text{SbF}_5/\text{SO}_2$ , the signal was temperature-dependent and broadened as the temperature was lowered. Both results are consistent with an equilibrium that is slow or near the NMR timescale. In the case of ethylene chloronium ion, the equilibrium is slow and the spectral signals for the asymmetric structure are resolved. In the case of the ethylene bromonium ion, the equilibrium is near the NMR timescale and the spectral signals are coalesced but broaden at low temperature due to a slowed equilibrium. Additional supporting evidence for the presence of an equilibrium includes temperature-dependent chemical shifts in 2,2-dimethylethylene bromonium ion [3] and nonadditive substituent effects on chemical shifts [2].

## COMPARATIVE HYPOTHESES

The data discussed above can be evaluated in the context of three hypotheses: isotope-induced desymmetrization, an equilibrium of asymmetric solvatomers, and an equilibrium of asymmetric ion- $\text{SO}_2$  complexes.

The most problematic data for the first two hypotheses are the dynamic NMR results from Olah's original characterizations. These data suggest the presence of equilibria in the absence of isotopes; and furthermore, they suggest the equilibria are near or even slow relative to the NMR timescale. Though isotope-induced desymmetrization provides a seemingly reasonable explanation for the isotopic perturbation of equilibrium studies, it does not account for the evidence of equilibria in the absence of isotopes. Likewise, an equilibrium involving asymmetric solvatomers can explain the isotopic perturbation of equilibrium data. But because the interconversion of solvatomers is reasonably faster than the NMR timescale, it does not explain the evidence of the appearance of NMR signals consistent with a static asymmetric structure.

Conversely, the latter hypothesis provides a simple direct chemical explanation for the experimental and computational evidence. An equilibrium involving ion- $\text{SO}_2$  complexes can be used to explain evidence for equilibria in the presence or absence of isotopes, and can be used to explain interconversion rates near the NMR timescale. Notwithstanding the correctness of this hypothesis, the significance and utility of first two hypotheses are not called into question. Though they may not apply in this specific case, they are general concepts that aid the understanding of the origin of isotope shifts and the role of solvation in determining symmetry.

## SUMMARY AND CONCLUSIONS

The observed isotope shifts in isotopically labeled tetramethylene halonium ions are consistent with a combination of intrinsic and equilibrium isotope shifts. The presence of equilibrium isotope shifts suggests that these ions exist as equilibria involving asymmetric ions. The initial interpretation of the structure of these ions as a rapid equilibrium of asymmetrically bridged halonium ions was later deemed incorrect. Gas-phase computational results refute the existence of asymmetrically bridged halonium ions or unbridged  $\beta$ -halocarbenium ions and favor the symmetric halonium ion. However, computational results also suggest that the experimental solvent is not inert and can form a covalent adduct. The resulting ion- $\text{SO}_2$  complexes are not symmetric halonium ions, asymmetrically bridged halonium ions, nor  $\beta$ -halocarbenium ions. We therefore postulate that the widely cited characterizations of symmetric 1,2-bridged halonium ions in superacidic solutions are erroneously assigned.

## ACKNOWLEDGMENTS

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