UC Riverside

UC Riverside Previously Published Works

Title

Hydrogen bonding versus hyperconjugation in condensed-phase carbocations.

Permalink

<https://escholarship.org/uc/item/90h407g9>

Journal

Organic & biomolecular chemistry, 11(23)

ISSN

1477-0520

Authors

Reed, Christopher A
Stoyanov, Evgenii S
Tham, Fook S

Publication Date

2013-06-01

DOI

10.1039/c3ob40737c

Peer reviewed

Hydrogen bonding versus hyperconjugation in condensed-phase carbocations†

Cite this: *Org. Biomol. Chem.*, 2013, **11**, 3797

Christopher A. Reed,* Evgenii S. Stoyanov and Fook S. Tham

Hyperconjugative stabilization of positive charge in tertiary carbocations is the textbook explanation for their stability and low frequency νCH bands in their IR spectra have long been taken as confirming evidence. While this is substantiated in the gas phase by the very close match of the IR spectrum of argon-tagged *t*-butyl cation with that calculated under C_s symmetry, the situation in condensed phases is much less clear. The congruence of $\nu\text{CH}_{\text{max}}$ of *t*-Bu⁺ in superacid media (2830 cm⁻¹) with that in the gas phase (2834 cm⁻¹) has recently been shown to be accidental. Rather, $\nu\text{CH}_{\text{max}}$ varies considerably as a function of counterion in a manner that reveals the presence of significant C–H...anion hydrogen bonding. This paper addresses the question of the relative importance of hyperconjugation versus H-bonding. We show by assigning IR spectra in the νCH region to specific C–H bonds in *t*-butyl cation that the low frequency $\nu\text{CH}_{\text{max}}$ band in the IR spectrum of *t*-butyl cation, long taken as direct evidence for hyperconjugation, appears to be due mostly to H-bonding. The appearance of similar low frequency νCH bands in the IR spectra of secondary alkyl carboranes such as *i*-Pr(CHB₁₁Cl₁₁), which have predominant sp³ centres rather than sp² centres (and are therefore less supportive of hyperconjugation), also suggests the dominance of H-bonding over hyperconjugation.

Received 12th April 2013,

Accepted 23rd April 2013

DOI: 10.1039/c3ob40737c

www.rsc.org/obc

Introduction

Carbocations, at least when tertiary, are generally accepted as reaction intermediates in nucleophilic substitution reactions and in acid-catalyzed reactions of hydrocarbons critically important to the petrochemical industry.¹ Following Olah's pioneering 1963 characterization of *t*-butyl cation by NMR in superacid media,² five decades of research on its stability and energetics has prompted the question: the final answer or a never ending story?³ The remarkably close coincidence of the experimental gas phase IR spectrum⁴ of argon-tagged *t*-Bu⁺ with that calculated^{3,5,6} under C_s symmetry (Fig. 1) suggests that we have indeed arrived at the final answer – at least for the gas phase. Hyperconjugative delocalization of positive charge predominantly *via* the three C–H bonds that are aligned with the formally vacant p_z orbital, is the textbook explanation for its stability.

In condensed phases, however, the situation is far from settled. Although the low frequency of $\nu\text{CH}_{\text{max}}$ in the IR spectrum of *t*-Bu⁺ in superacid media (2830 cm⁻¹), long taken as evidence of hyperconjugation,⁷ nearly coincides with that in the gas phase (2834 cm⁻¹),⁴ this coincidence has recently been

Fig. 1 The C_s symmetry structure of gas phase *t*-Bu⁺ showing hyperconjugative alignment of three of the C–H bonds with the formally vacant p_z orbital on the planar central C atom.

shown to be accidental.⁸ In fact, the experimental value of $\nu\text{CH}_{\text{max}}$ varies considerably as a function of counterion, by up to 90 cm⁻¹. Moreover, the $\nu\text{CH}_{\text{max}}$ values of *t*-Bu⁺ salts correlate linearly with anion basicity on the νNH scale⁹ providing strong evidence for the presence of C–H...anion H-bonding. Indeed, there is considerable evidence of C–H hydrogen bonding in compounds having various degrees of acidity in their C–H bonds,^{10–13} including arenium ions.⁸ So, while the low frequency of $\nu\text{CH}_{\text{max}}$ has been taken as *prima facie*⁷ and continuing⁴ evidence for C–H bond hyperconjugation in condensed media, C–H hydrogen bonding to the environment presents an alternative explanation.

Both hyperconjugation and C–H hydrogen bonding result in C–H bond weakening and lowered νCH frequencies. The challenge is to separate the two effects. Herein, we begin to address this question and come to the surprising conclusion

Department of Chemistry, University of California, Riverside, California 92651, USA.
E-mail: chris.reed@ucr.edu; Fax: +1(951)827 2027

†Electronic supplementary information (ESI) available: IR spectra of carbocationic carboranes. See DOI: 10.1039/c3ob40737c

Fig. 2 Icosahedral carborane anions of the type $\text{CHB}_{11}\text{X}_{11}^-$ and $\text{CHB}_{11}\text{R}_5\text{X}_6^-$ used in this work (abbrev. $\{\text{X}_{11}^-\}$ and $\{\text{R}_5\text{X}_6^-\}$ respect).

that the low frequency $\nu_{\text{CH}_{\text{max}}}$ value may be due almost entirely to hydrogen bonding rather than hyperconjugation.

We choose carboranes¹⁴ (Fig. 2) as counterions in carbocation salts because their low basicity and exceptionally high stability imparts room temperature (and often higher) stability to their carbocation salts.^{15,16}

Experimental

All sample handling was carried out under an inert atmosphere (H_2O , O_2 < 1 ppm). $t\text{-Bu}^+\{\text{Cl}_{11}^-\}$ was obtained *via* decomposition of the diethylchloronium salt $\text{Et}_2\text{Cl}^+\{\text{Cl}_{11}^-\}$ at 150 °C.¹⁶ Similarly, the 2,3-dimethylbutyl cation was obtained by the interaction of 2-chloropropane with freshly sublimed $\text{H}\{\text{Cl}_{11}\}$ acid¹⁴ resulting in the formation of the di-*i*-propyl chloronium salt $\text{Pr}_2\text{Cl}^+\{\text{Cl}_{11}^-\}$, which was decomposed at 100 °C in accordance with eqn (1):

The white solid was washed with cold dichloromethane and dried under vacuum. $t\text{-Bu}^+\{\text{Br}_{11}^-\}$ was obtained in a similar manner from 1-chlorobutane and $\text{H}\{\text{Br}_{11}\}$. IR spectra of $t\text{-Bu}^+\{\text{Me}_5\text{Cl}_6^-\}$ and $t\text{-Bu}^+\{\text{Me}_5\text{Br}_6^-\}$ were obtained earlier.¹⁵

Other carbocations with $\{\text{Cl}_{11}^-\}$ as counterion were obtained directly inside the IR cell by interaction of excess solid $\text{H}\{\text{Cl}_{11}\}$ acid with the appropriate chlorocarbon: 1-chlorobutane, 2-chloropropane, *t*-butyl chloride, chloro-*cyclo*-butane, 2-chloro-2-methylbutane, chloro-*cyclo*-pentane and chloro-*cyclo*-hexane. Solid $\text{H}\{\text{Cl}_{11}\}$ acid was placed on the top surface of the diamond crystal of the attenuated total reflectance (ATR) IR accessory and wetted with a small drop of liquid chlorocarbon that was not sufficient for full acid utilization. Running the spectrum without applied pressure allowed investigation of the oily byproduct on the diamond surface. Running the spectrum of the solid particles crushed under pressure, which contained the carbocation salt, allowed their spectra to be obtained with minor overlap from the spectra of byproducts. Computer subtraction of the byproduct spectrum and excess acid allowed isolation of good quality carbocation spectra. The $\{\text{Cl}_{11}^-\}$ salt of 1-adamantyl cation was obtained by stirring $\text{H}\{\text{Cl}_{11}\}$ with a CCl_4 solution of 1-chloroadamantane following by CCl_4 washing of the precipitate.

IR spectra were run on a Perkin Elmer Spectrum-100 spectrometer in the 4000–400 cm^{-1} frequency range in transmission mode as KBr pellets or in attenuated total reflectance mode. Spectra were manipulated using GRAMMS/A1 (7.00) software from Thermo Scientific.

Results and discussion

Assignment of ν_{CH} in $t\text{-Bu}^+$

The interpreted IR spectrum of $t\text{-Bu}^+$ in the gas phase⁴ under C_s symmetry is the point of departure for assigning the spectrum in the solid phase. This is justified by the finding that the high resolution X-ray structure of $[t\text{-Bu}^+][\text{CHB}_{11}\text{Cl}_{11}^-]$ ⁸ where the H atom positions were located with reasonable certainty, and more recently $[t\text{-Bu}^+][\text{Al}_2\text{Br}_7^-]$,¹⁷ shows the cation to have near C_s symmetry (Fig. 3). Unlike the gas phase, however, the H atom positions in $[t\text{-Bu}^+][\text{CHB}_{11}\text{Cl}_{11}^-]$ are all in crystallographically distinct environments and therefore could give rise to up to nine ν_{CH} bands. Each C–H bond has interactions with one or two Cl atoms of the anion. H...Cl distances lie in the range 2.91–3.32 (the sum of the van der Waals radii is 2.95 Å) with C–H...Cl angles 120–180°. These are consistent with hydrogen bonding.^{8,11,12,18}

In the gas phase spectrum of $t\text{-Bu}^+$, the ν_{CH} vibrations give rise to three observed bands at 3036, 2965 and 2834 cm^{-1} .⁴ The two highest frequency bands can be assigned to ν_{asym} and ν_{sym} arising from the six minimally-hyperconjugated C–H groups. The lowest frequency band is assigned to the three maximally-hyperconjugated C–H groups.

In the solid phase structure (Fig. 3), two of the three C–H bonds that are aligned for maximal hyperconjugation, C2–H2C and C4–H4C, have regular (*i.e.* mono-furcated) H-bonding interactions with Cl atoms of the counterion, *i.e.* C–H...Cl angles >160°. Because of hyperconjugation *and* optimal hydrogen bonding, they are expected to have the strongest H-bonds

Fig. 3 X-ray structure of $t\text{-Bu}^+$ as $\text{CHB}_{11}\text{Cl}_{11}^-$ salt showing approximate C_s symmetry of the cation along with H-bonding cation–anion contacts within H-bonding range.

and give rise to the lowest frequency bands.⁹ The third C–H bond aligned for maximal hyperconjugation (C3–H3A) and all six of the H atoms whose C–H bonds are minimally aligned for hyperconjugation have varying degrees of weaker hydrogen bonding and their νCH bands are therefore expected at higher frequencies. They all have C–H...Cl angles in the range 120–160°, somewhat more acute than optimal for mono-furcated H-bonding.¹⁸ Most are bi-furcated but two (at H4A and H4B) are mono-furcated. Thus, an overall 2:1:6 grouping of three types of νCH bands might be expected. Fewer bands will be observed if there are accidental overlaps of these groups. More bands may appear if the strength of H-bonding is sufficiently variable.

The solid phase IR spectrum of $[t\text{-Bu}^+][\text{CHB}_{11}\text{Cl}_{11}^-]$ in the νCH region is shown in Fig. 4 along with the peak-enhanced spectrum after applying a Gaussian-shaped deconvolution to help separate the band maxima. The weak, lowest frequency band at 2750 cm^{-1} is assigned to the two mono-furcated H-bonded, C–H bonds that are optimally aligned for hyperconjugation. The ν_{max} band at 2791 cm^{-1} is assigned to the six C–H bonds that are minimally-aligned for hyperconjugation. They mostly show weaker bi-furcated H-bonding. The ν_{max} band may also contain the νCH arising from the remaining (third) C–H bond (C3A–H3) aligned for maximal hyperconjugation but which has only bifurcated H-bonding. Because the strength of H-bonding varies for all seven C–H bonds, ν_{max} may be split and contribute to the somewhat higher frequency weak shoulders at 2826 and 2856 cm^{-1} . The highest frequency bands at 2890 and 2954 cm^{-1} lie in the region typical of C–H bonds removed from proximity to positive charge and are assigned to impurities in the synthesis, arising from traces of higher carbocations arising from carbocationic oligomerization, or possibly to $t\text{-Bu}^+$ that is deprived of anion interactions due to surface effects.

Fig. 4 (a) IR spectrum of solid $[t\text{-Bu}^+][\text{CHB}_{11}\text{Cl}_{11}^-]$ in the νCH region and (b) the deconvolution-enhanced spectrum.

The most important conclusion resulting from these assignments is that $\nu\text{CH}_{\text{max}}$ arises almost entirely from C–H bonds that are minimally aligned for hyperconjugation. Under precise C_s symmetry, the six non-hyperconjugatively-aligned C–H bonds that would be the major (or sole) contributors to this band are symmetry-forbidden from engaging in hyperconjugative stabilization. Under the *near* C_s symmetry existent in the crystal, hyperconjugative overlap will be non-zero. The assignment of $\nu\text{CH}_{\text{max}}$ to the C–H bonds that are minimally aligned for hyperconjugation suggests that its low frequency may be mainly the result of C–H hydrogen bonding.

Further insight can be obtained from the intercept of the plot of $\nu\text{CH}_{\text{max}}$ versus anion basicity on the νNH basicity scale. The $\nu\text{NH} = 0 \text{ cm}^{-1}$ value on the νNH basicity scale corresponds to a CCl_4 solvent-separated $\text{R}_3\text{N}^+\text{H}\cdots(\text{CCl}_4)\cdots\text{anion}$ ion pair.⁹ In order to relate the data to gas phase $t\text{-Bu}^+$ ion, the abscissa origin should coincide with νNH in a vacuum. This was estimated by comparing the νNH frequencies of $\text{Oct}_3\text{NH}^+\cdots\text{CCl}_4$ and Oct_3NH^+ *in vacuo* as calculated by DFT at the B3LYP/6-31G** level, giving 3424 and 3376 cm^{-1} respectively. Their difference makes -48 cm^{-1} the correct abscissa origin. When the $\nu\text{CH}_{\text{max}}$ values of $t\text{-Bu}^+$ for five different carborane salts are plotted against anion νNH (Fig. 5, red), linearity is observed, confirming their dependence on C–H hydrogen bonding.⁸ When fitted to a least squares linear regression analysis and extrapolated to vacuum, the intercept is $\nu\text{CH} = 2953 \pm 4 \text{ cm}^{-1}$. This is very close to the $\nu\text{CH}_{\text{sym}}$ value of 2965 cm^{-1} for the six non-hyperconjugated C–H bonds in the gas phase spectrum,⁴ providing additional evidence that H-bonding may be the predominant reason for the low frequency of $\nu\text{CH}_{\text{max}}$.

Let us now consider the lowest frequency νCH band (*i.e.* shoulder) at 2745 cm^{-1} that is assigned to the vibrations of the two C–H bonds that are aligned correctly for hyperconjugation and which have relatively strong, mono-furcated H-bonds to

Fig. 5 Plot of $\nu\text{CH}_{\text{max}}$ (red) and $\nu\text{CH}_{\text{low}}$ (black) of $t\text{-Bu}^+$ vs. νNH anion basicity values with least squares linear regression analyses: **1** = $\{\text{Cl}_{11}^-\}$ 3163 cm^{-1} , **2** = $\{\text{Me}_5\text{Cl}_6^-\}$ 3143, **3** = $\{\text{Br}_{11}^-\}$ 3140, **4** = $\{\text{Br}_6^-\}$ 3125, **5** = $\{\text{Me}_5\text{Br}_6^-\}$ 3120 cm^{-1} . The green points are the gas phase values for $\nu\text{CH}_{\text{hyperconj}}$ (2834 cm^{-1}) and $\nu\text{CH}_{\text{non-hyperconj}}$ (2965 cm^{-1}) from ref. 4.

the anion (C2–H2C and C4–H4C in Fig. 3). We label this band $\nu\text{CH}_{\text{low}}$. As previously discussed,⁸ the angular dimensions of these methyl groups in the X-ray structure are similar to those of the gas phase ion, providing structural support for hyperconjugation, namely: the C–C–H angles of the vertically aligned C–H bonds (101–103°) have become acute at the expense of the two non-hyperconjugated C–H bonds (113–117°). Indeed, it has been argued⁶ that the adoption of C_s symmetry by $t\text{-Bu}^+$ is driven by maximization of hyperconjugative stabilization and this is supported by the appearance of approximate C_s symmetry in the solid state cation. Do the IR results on $\nu\text{CH}_{\text{low}}$ give insight into the question of hyperconjugation *vs.* H-bonding for C2–H2C and C4–H4C?

Experimentally, there are fewer data to consider than with $\nu\text{CH}_{\text{max}}$. Of the five $t\text{-Bu}^+$ salts studied, only three show a discernible low frequency $\nu\text{CH}_{\text{low}}$ shoulder. These are the $\{\text{Cl}_{11}^-\}$, $\{\text{Br}_{11}^-\}$ and $\{\text{Br}_6^-\}$ salts and their $\nu\text{CH}_{\text{low}}$ frequencies are plotted in Fig. 5 (black). Without high resolution X-ray (or neutron) diffraction data it is difficult to understand the reasons for the absence of this shoulder in the $\{\text{Me}_5\text{Br}_6^-\}$ and $\{\text{Me}_5\text{Cl}_6^-\}$ salts but presumably crystal packing effects do not lead to strongly mono-furcated H-bonds. Nevertheless, the following arguments indicate that even with the limited IR data in hand, H-bonding contributes to the low frequency of these shoulders.

Firstly, even though more data would be desirable, the apparent linearity of the correlation of $\nu\text{CH}_{\text{low}}$ with νNH suggests a strong influence from H-bonding, just as it was with $\nu\text{CH}_{\text{max}}$. Secondly, a least squares regression analysis extrapolates to an intercept at $2989 \pm 10 \text{ cm}^{-1}$ which, although having a significant standard deviation, is far from the gas phase value of 2834 cm^{-1} determined for truly hyperconjugated C–H bonds *in vacuo*.⁴ Thirdly, the slope is nominally somewhat *greater* than that of the $\nu\text{CH}_{\text{max}}$ line, suggesting an even greater dependence on H-bonding. However, given the error limits of an extrapolation from just three datum points, it is safer to conclude simply that the slope is similar to that of $\nu\text{CH}_{\text{max}}$, which, as shown above, is dependent on H-bonding. Thus, the IR data on $\nu\text{CH}_{\text{low}}$ indicate that it too is significantly dependent on H-bonding. This is an expected result if hyperconjugation is present because hyperconjugation increases positive charge on the three C–H bonds that are aligned with the empty p_z thereby making them better H-bond donors. There is another consideration, however. With the participation of the other six C–H bonds in H-bonding and dispersal of positive charge *via* a σ -bond polarization mechanism, the necessity of charge delocalization *via* hyperconjugation may be diminished, relative to that in the gas phase.

Other carbocations

In the primary/secondary/tertiary sequence $\text{Me}\{\text{Cl}_{11}^-\}$, $\text{Et}\{\text{Cl}_{11}^-\}$, $\text{i-Pr}\{\text{Cl}_{11}^-\}$ and $t\text{-Bu}^+\{\text{Cl}_{11}^-\}$ the covalent character of the $\text{R}-\{\text{Cl}_{11}\}$ bond decreases as its ionicity increases until in the tertiary system it has fully ionic sp^2 carbocation character. If hyperconjugation was the sole cause of low frequency νCH IR bands, such bands should only appear in tertiary systems

Table 1 IR frequencies of νCH bands arising from CH bonds α to positive charge (marked in red) in secondary and tertiary systems

Cation-like moiety or cation	Anion	νCH ($\nu\text{CH}_{\text{max}}$ bold)
$\{\text{Cl}_{11}^-\}$		2780
$\{\text{Cl}_{11}^-\}$		2781
$\{\text{Cl}_{11}^-\}$		2779
$\{\text{Cl}_{11}^-\}$		2791	2750
	$\{\text{Me}_5\text{Cl}_6^-\}$	2807	2770	
	$\{\text{Me}_5\text{Br}_6^-\}$	2766	2733	
	$\{\text{H}_5\text{Br}_6^-\}$		2757	2688
	$\{\text{Br}_{11}^-\}$		2768	2725
$\{\text{Cl}_{11}^-\}$		2786	
	$\{\text{Me}_5\text{Br}_6^-\}$		2786	2677
$\{\text{Cl}_{11}^-\}$	2870	2798	2740
	$\{\text{Cl}_{11}^-\}$		2711
$\{\text{Me}_5\text{Br}_6^-\}$	2730	2693	2654
1-Adamantyl ⁺	$\{\text{Cl}_{11}^-\}$		2857	2840

with sp^2 central C atoms because only in such planar carbocations can significant hyperconjugative overlap occur. However, as shown in Table 1, we observe a low frequency νCH band in the secondary $\text{i-Pr}\{\text{Cl}_{11}\}$ system. From the X-ray structure of $\text{i-Pr}(\text{CHB}_{11}\text{Me}_5\text{Br}_6)$,¹⁵ we know that *i*-propyl carborane compounds do not have ionic structures (even though they can show *ion-like* reaction chemistry). The central C atom is pyramidal and tetracoordinate, showing predominant sp^3 character, and is covalently bound to a halogen atom of the carborane anion. So hyperconjugative stabilization is presumably minimal. The explanation for the low-frequency νCH band would seem therefore to lie in hydrogen bonding rather than hyperconjugation. Evidently, there is enough charge separation in a secondary $\text{R}-\{\text{Cl}_{11}\}$ bond to trigger strong H-bonding with counterions in the solid state. This is borne out by the appearance of almost identical low frequency bands in two other secondary carbocation-like species: *cyclo*-butyl and *cyclo*-pentyl carboranes (Table 1). The frequencies of these bands are very close to that of $\nu\text{CH}_{\text{max}}$ in *t*-butyl cation, consistent with hyperconjugation making minimal contribution to this band in either secondary or tertiary systems.

Three tertiary carbocations that are structurally related to $t\text{-Bu}^+\{\text{Cl}_{11}^-\}$ all show an intense $\nu\text{CH}_{\text{max}}$ band within *ca.* 10 cm^{-1} of that in $t\text{-Bu}^+$: neopentyl, 2,3-dimethylbutyl and methyl-*cyclo*-pentyl cations (Table 1). Those with β methylene groups all show νCH bands in the normal alkane frequency region ($2850\text{--}2980 \text{ cm}^{-1}$), unaffected by positive charge. This

indicates that the C–H bonds responsible for the low frequency bands are α to the carbocationic center.

In addition to a $\nu\text{CH}_{\text{max}}$ band, some compounds show additional weaker bands or shoulders at somewhat lower and/or higher frequencies (Table 1). These can be understood in terms of a range of H-bond types varying between mono-, bi- and tri-furcated interactions with the anion.

The spectrum of the methyl-*cyclo*-pentyl cation is distinctive. Depending on the counterion, its $\nu\text{CH}_{\text{max}}$ band occurs some 40–80 cm^{-1} lower in frequency than that in the corresponding *t*-Bu⁺ salts. Moreover, the bandwidth is narrower and there are no significant shoulders. The lower frequency suggests that H-bonding to the anion is particularly strong, presumably dominated by mono-furcated H-bonds rather than weaker bi-furcated H-bonds. The narrower bandwidth suggests that all H-bonds are of similar strength (or that the band is dominated by stretches of unusually high intensity).

Finally, we have recorded the IR spectrum of the 1-adamantyl cation as a {Cl₁₁[−]} salt. It shows no particularly low frequency νCH bands, only bands at 2936m, 2912s and 2857m cm^{-1} . This is the expected result if, as is widely accepted, ring constraints take the C–H bonds out of alignment for hyperconjugation and positive charge is delocalized *via* C–C bond (rather than C–H bond) hyperconjugation. Apparently, with significant C–C bond hyperconjugation, there is insufficient positive charge buildup at the α C–H bonds for significant H-bonding to occur.

Conclusion

Without doubt, hyperconjugation is an important internal mechanism for positive charge delocalization in gas phase carbocations. But in condensed phases, external delocalization of positive charge to the environment *via* C–H hydrogen bonding is so prevalent that hyperconjugation may be less important. Certainly, the low frequency $\nu\text{CH}_{\text{max}}$ band in the IR spectrum of *t*-butyl cation and other carbocations, long taken as evidence for hyperconjugation, appears to be due mostly to H-bonding because it is assigned to the six C–H bonds that are minimally aligned for hyperconjugation. The relative contributions of hyperconjugation and H-bonding to the low-frequency shoulder on this band, assigned to the three C–H that are maximally aligned for hyperconjugation, are difficult to partition.

A relevant observation is the lack of red-shifting IR evidence for H-bonding in chemically related cations. The dimethyl-chloronium ion,¹⁶ (CH₃)₂Cl⁺, shows a slight *blue* shift in $\nu_{\text{asym}}\text{CH}$ relative to CH₃Cl and the trimethyloxonium ion,¹⁹ (CH₃)₃O⁺, shows $\nu_{\text{asym}}\text{CH}$ quite close to that of Et₂O. Neither shows the large decrease observed with *t*-Bu⁺ cation. Fundamental differences between red- and blue-shifted H-bonds have not been found²⁰ but these observations suggest that carbocations are different from cations of the more electronegative elements and that hyperconjugation is that difference.

The presence of C–H hydrogen bonding is a reminder that carbocations are strong acids. Because of their kinetic instability towards cationic alkene oligomerization, the thermodynamic acidities of carbocations are difficult to quantify, particularly in dilute solution. The νNH basicity scale applied to π systems²¹ indicates that protonated alkenes (*i.e.* carbocations) are stronger acids than protonated alkynes (*i.e.* vinyl cations) but weaker acids than protonated arenes (*i.e.* arenium ions). In a [Bu⁺][Al₂Cl₇[−]] melt, the acidity of *t*-Bu⁺ is apparently higher and is said to equate with that of 100% H₂SO₄, the threshold of superacidity.¹⁷

H-bonding in carbocations has only recently become appreciated. Its importance in directing the outcome of terpene biosynthesis has been stressed by Tantillo.^{22,23} H-bonding to C–H bonds α to positively charged C provides models for second stage of the E1 elimination mechanism²⁴ and the experimental points can be taken as early snapshots along the E1 potential energy surface.

Abbreviations

{Cl ₁₁ [−] }	CHB ₁₁ Cl ₁₁ [−]
{Me ₅ Cl ₆ [−] }	CHB ₁₁ Me ₅ Cl ₆ [−]
{Br ₁₁ [−] }	CHB ₁₁ Br ₁₁ [−]
{H ₅ Br ₅ [−] }	CHB ₁₁ H ₅ Br ₆ [−]
{Me ₅ Br ₆ [−] }	CHB ₁₁ Me ₅ Br ₆ [−]

Acknowledgements

We thank Prof. Mark Juhasz for assistance and the National Science Foundation (CHE 1144838) and the National Institutes of Health (GM 23851) for generous support.

Notes and references

- (a) G. A. Olah and A. Molnar, *Hydrocarbon Chemistry*, John Wiley & Sons, N.Y., 2003; (b) *Stable Carbocation Chemistry*, ed. G. K. S. Prakash and P. v. R. Schleyer, John Wiley & Sons, N.Y., 1997; (c) *Carbocation Chemistry*, ed. G. A. Olah and G. K. S. Prakash, John Wiley & Sons, Hoboken, N.J., 2004.
- G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien and E. B. Baker, *J. Am. Chem. Soc.*, 1963, **85**, 1328.
- H. Feng, W. Sun, Y. Xie and H. F. Schaefer III, *Chem.–Eur. J.*, 2011, **17**, 10552.
- G. E. Doublerly, A. M. Ricks, B. W. Ticknor, P. v. R. Schleyer and M. A. Duncan, *J. Am. Chem. Soc.*, 2007, **129**, 13782.
- S. Sieber, P. Buzek, P. v. R. Schleyer, W. Koch and J. W. de M. Carneiro, *J. Am. Chem. Soc.*, 1993, **115**, 259.
- G. Rasul, J. L. Chen, G. K. S. Prakash and G. A. Olah, *J. Phys. Chem. A*, 2009, **113**, 6795.
- G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre and I. J. Bastien, *J. Am. Chem. Soc.*, 1964, **86**, 1360.

- 8 E. S. Stoyanov, I. V. Stoyanova, F. S. Tham and C. A. Reed, *Angew. Chem., Int. Ed.*, 2012, **51**, 9149.
- 9 E. S. Stoyanov, K.-C. Kim and C. A. Reed, *J. Am. Chem. Soc.*, 2006, **128**, 8500.
- 10 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.
- 11 D. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1990, 454.
- 12 T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48.
- 13 J. P. Lorand, *J. Phys. Org. Chem.*, 2011, **24**, 267.
- 14 C. A. Reed, *Acc. Chem. Res.*, 2010, **43**, 128.
- 15 T. Kato and C. A. Reed, *Angew. Chem., Int. Ed.*, 2004, **43**, 2908.
- 16 E. S. Stoyanov, I. V. Stoyanova, F. S. Tham and C. A. Reed, *J. Am. Chem. Soc.*, 2010, **132**, 4062.
- 17 F. Scholz, D. Himmel, H. Scherer and I. Krossing, *Chem.-Eur. J.*, 2013, **19**, 109.
- 18 J.-A. van den Berg and K. R. Seddon, *Cryst. Growth Des.*, 2003, **3**, 643.
- 19 R. F. Howe and M. J. Taylor, *Spectrochim. Acta, Part A*, 1987, **43**, 73.
- 20 S. Scheiner and T. Kar, *J. Phys. Chem. A*, 2002, **106**, 1784–1789.
- 21 E. S. Stoyanov, I. V. Stoyanova and C. A. Reed, *Chem.-Eur. J.*, 2008, **14**, 7880.
- 22 M. D. Bojin and D. J. Tantillo, *J. Phys. Chem. A*, 2006, **110**, 4810–4481.
- 23 Y. J. Hong and D. J. Tantillo, *Chem. Sci.*, 2013, DOI: 10.1039/c3sc50571e, advance article.
- 24 S. Gronert, *Acc. Chem. Res.*, 2003, **36**, 848–857.