PERKIN 2

C–H Hyperconjugation in α-chlorocarbocations

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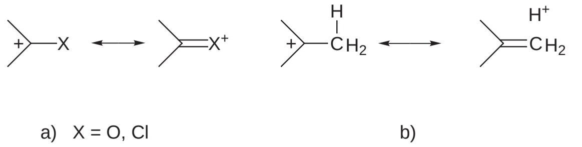
The lowering of C$_\beta$–H stretching frequencies in carbocations **1a**–**d** and **2a**–**c** induced by hyperconjugation was tested as a possible probe for estimating the electron donating ability of α-substituents. Conclusions are based on the results of high level quantum chemical calculations confirmed with experimental FT-IR spectra. Because the decrease in the C$_\beta$–H stretching frequency is comparable in **1b** and in **1c**, and in **2b** and **2c** respectively, it follows that α-substitution by a methyl group or by chlorine stabilizes a carbocation with almost the same effectiveness.

Introduction

The stability of carbocations depends on the type of atoms and atomic groups attached to the positive carbon atom and on steric restrictions imposed by sp^3–sp^2 rehybridization. The simplest carbocation, $CH_3{}^+$ is the least stable and in the gas phase[1] it has only recently been experimentally accessible. The order of stability of simple alkyl cations is 3° > 2° > 1° and is practically independent of the mode of their generation in the gas phase or in solution. Major factors governing the stability of carbocations are hyperconjugation, steric and field effects. Resonance effects are important in alkenyl and aryl substituted cations. In molecular orbital terms, hyperconjugation is described as the interaction between the vacant p-type orbital on the cationic center and the *pseudo* π-orbital of the adjacent C–H or C–C bond. The energy of this interaction depends on the square of the Fock matrix element between the donor and acceptor orbitals which is in turn a function of the dihedral angle and the type of donor σ-(pseudo-π) orbital.[2] A better overlap between the hyperconjugating σ orbital with the empty p orbital leads to a shortening of the C_{sp^2}–C_{sp^3} bond and a lengthening of the properly oriented adjacent CH (CC) bond. On the other hand charge delocalization reduces the electron donation of the hyperconjugating orbital which affects the change in the C_{sp^2}–C_{sp^3} bond length in the opposite direction. Recent crystallographic studies by Laube *et al.*[3] on cumyl hexafluoroantimonate provide strong support for the effect of phenyl delocalization on C^+–C bond lengths and hyperconjugative interactions.

Electronegative heteroatoms attached directly to the cationic carbon increase the stability of the ion by the so called α-effect and explain, *inter alia*, the higher solvolytic reactivity of α–halo ethers.[4] Thus, the methoxymethyl cation has been isolated as a solid salt, $CH_3OCH_2{}^+$ $SbF_6{}^-$. This effect is ascribed to the contribution of a second resonance structure as in Scheme 1a.



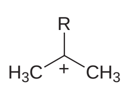
a) X = O, Cl

b)

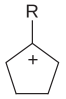
Scheme 1

Crystal structure analysis of α-chlorosubstituted carbocations by Laube *et al.*[5] suggests the presence of a partial C=Cl double bond character, a conclusion supported by *ab initio* calculations and NMR[6a–c] and IR[6d–g] spectroscopic data. Of the two effects exhibited by the electronegative chlorine atom, *i.e.* the destabilizing inductive and stabilizing resonance effect, the latter is more pronounced. The electron back-donation by the chlorine atom is isoelectronic with hyperconjugation (Scheme 1). A similar intramolecular electron density transfer in the two cases is manifested by comparable ^{13}C NMR chemical shifts in corresponding α-CH_3 and α-Cl substituted carbocations.[7] Moreover, the barrier of the *cis–trans* isomerization of methyl or chloro substituted allyl cations has been calculated to be almost equal.[6f]

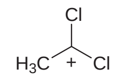
The objective of the research described in this paper was to further investigate the relationship between hyperconjugation and the α-chlorine effect in simple carbocations. The hyperconjugative effect of a neighboring C–H bond can be easily recognized in the IR spectrum of carbocations generated in cryogenic SbF_5 matrices. We have shown that the C–H stretching frequency in the methylcyclopentyl cation is 2775 cm^{-1} *i.e.* about 200 cm^{-1} lower than the average C–H frequency in saturated hydrocarbons (2950 cm^{-1}).[8a] In contrast, in the *tert*-butyl cation[9] with three adjacent methyl groups the C–H frequency is lowered to 2845 cm^{-1}. Taking cation **1** as a model (R = H, CH_3, Cl) the hyperconjugative shift of a C$_\beta$–H bond will depend on electron donating properties of the substituent R. With a better donor, the electron demand from the C–H bond is smaller and the change in the C$_\beta$–H stretching frequency is less pronounced (*vide supra*). Accordingly, the frequency of the C$_\beta$–H bond may be used as a measure of stabilization of a carbocation by substituent R. In order to test this hypothesis the C–H stretching frequencies of two series of carbocations (**1a**–**d** and **2a**–**c**) were calculated by density functional theory and compared with experimentally observed frequencies of the respective cations generated in cryogenic SbF_5 matrices (Table 1).



1a: R = H
1b: R = CH_3
1c: R = Cl



2a: R = H
2b: R = CH_3
2c: R = Cl



1d

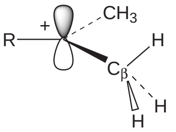
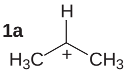
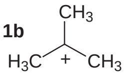
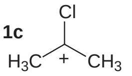
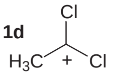
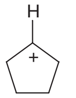
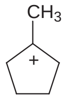
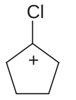


Table 1 C_β–H stretching vibrations affected by hyperconjugation

	$\nu_{C\beta\text{-}H}$/cm^{-1}		
	Calc.	Scaled[a]	Experimental
1a 	2888	2776	2730
1b 	2974	2859	2845
1c 	2965	2851	2845
1d 	2981	2865	—
2a 	2820	2711	—
2b 	2902	2789	2765
2c 	2934	2820	2780

[a] Scaling by a factor of 0.9614, see ref. 10*c*.

Results and discussion

Structures and IR active vibrational frequencies of cations **1a**–**1d**, and **2a**–**2c** were calculated by the density functional method at B3-LYP/6-31G(d) level.[10] Full geometry optimizations were performed for all cations and the obtained structures were genuine minima on potential energy surfaces as demonstrated by the absence of imaginary vibrational frequencies. The selected experimentally observed C_β–H stretching vibrations affected by hyperconjugation (Table 1) appear as signals of lowest frequencies in the C–H stretching region. The decrease in these frequencies is almost the same in methyl as in chloro substituted cations. However, both differ by about 100 cm^{-1} from the corresponding values in parent 2-propyl[9] and cyclopentyl cations.[8b]

Changes in calculated bond lengths (Fig. 1) also support the assumption that chlorine and methyl groups have similar stabilizing effects. The C_β–H bonds suitably positioned for hyperconjugation in **1b** and **1c** are almost equally elongated relative to **1a** (1.1077 and 1.1081 Å, respectively). Introduction of two chlorine atoms, as in **1d** leads merely to a discrete lengthening of the C_β–H bond to 1.0926. However, in **1a** these bonds are significantly longer (1.1175 Å). Similarly, the C_β–H bond in the chlorine derivative **2c** (1.1111 Å) is only marginally shorter than in the methyl substituted cation **2b** (1.1134 and 1.1152 Å, respectively). The hyperconjugatively shortened C^+–C_β bonds in all substituted cations are approximately 1.47 Å long, *i.e.* 0.03 Å longer than in the parent cation **1a**. By using the Reindl–Clark–Schleyer relationship[11] it is possible to calculate the hyperconjugation energy (E_{hyp}) from the known C^+–C_β bond length. Applying this relationship, the estimated E_{hyp} is 21 kcal mol^{-1} for the substituted cations, compared to 24 kcal mol^{-1} for the parent ion **1a**. The difference in the E_{hyp} values (3 kcal mol^{-1}) corresponds to a difference of 100 cm^{-1} (*vide supra*) in the hyperconjugative red shift of C_β–H stretching frequencies. A decrease in the C_β–H frequency of approximately 33 cm^{-1} corresponds to a hyperconjugation energy of 1 kcal mol^{-1}.

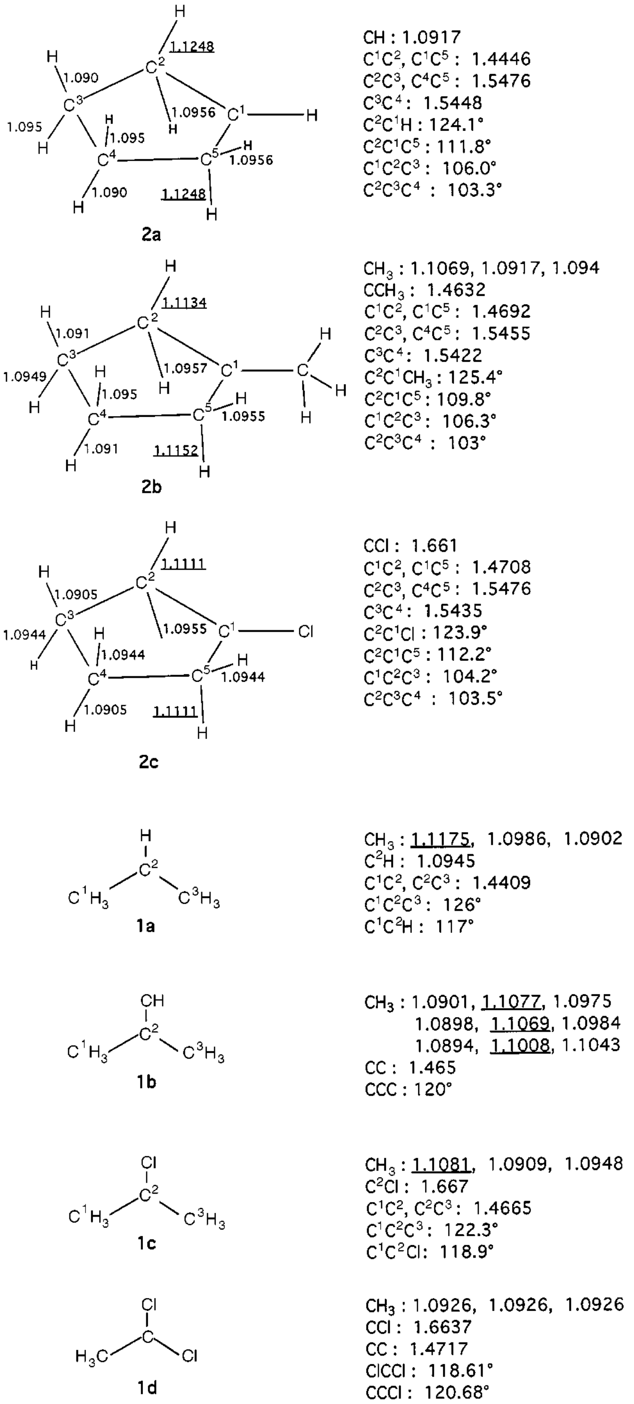


Fig. 1 Geometries of cations **1a**–**1d** and **2a**–**2c** calculated by B3-LYP/6-31G(d). Bond lengths in Å; bond angles in degrees. Structures reflect connections only. C–H bond distances lengthened by hyperconjugation are underlined.

Comparison with the experimental spectra

In most experiments the ionization started in the temperature range between 110 and 180 K. Since under the applied experimental conditions it was not possible to get better spectra of the cations, all the experimental data were obtained repetitively in a series of experiments. By our experience, the solid SbF_5 matrix material does not possess the best optical quality and the transparency of the matrix is highly sensitive to changes in temperature. This is reflected in a remarkable change of the spectral baseline, especially in the 2500–3500 cm^{-1} region. It is

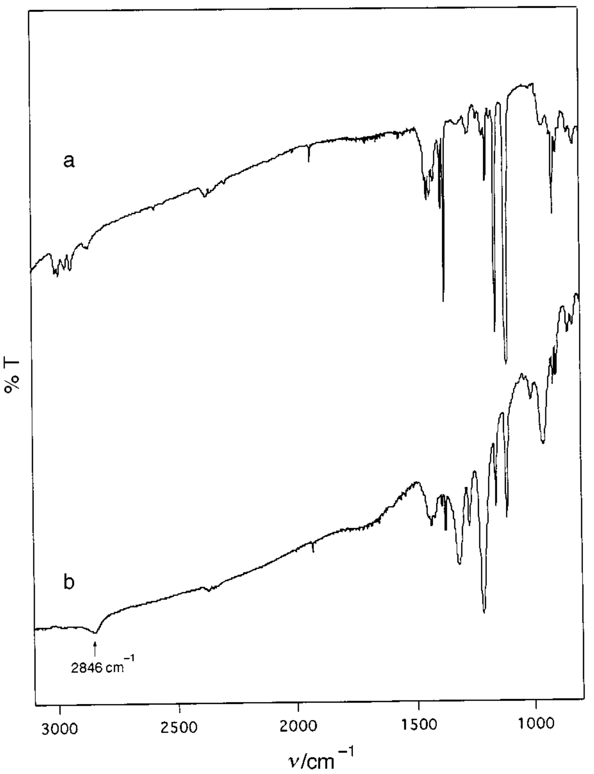


Fig. 2 FT-IR spectra of 2,2-dichloropropane-SbF$_5$ matrix a) at 77 K and b) at 240 K.

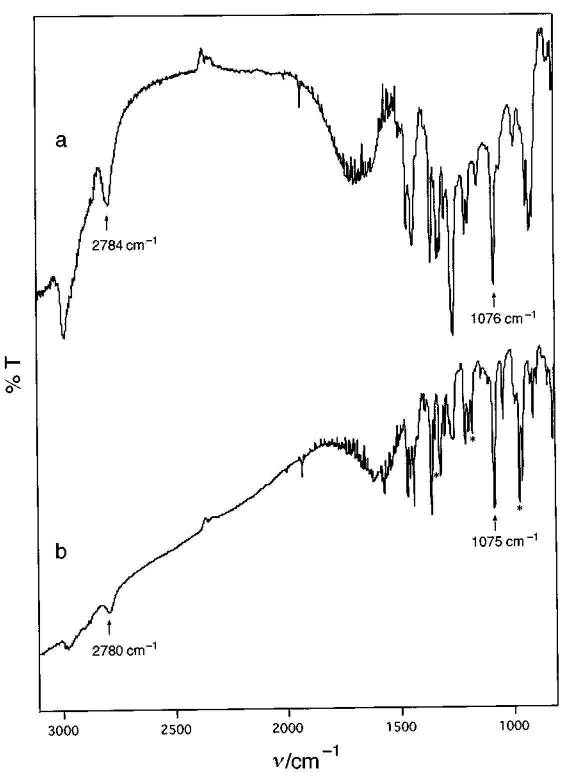


Fig. 3 FT-IR spectra of the 1-chloro-1-cyclopentyl cation prepared at 200 K a) from 1,2-dichlorocyclopentane, b) from 1,1-dichlorocyclopentane. Impurities are labeled with *.

known that even in the argon matrix, there are difficulties in recording the C–H stretching region because of the low intensity of the signals. The structures of the ions obtained under such experimental conditions are confirmed by comparison with the calculated frequencies. After scaling the C–H stretching frequencies by a recommended factor of 0.9614,[10c] a satisfactory agreement between the calculated and experimental spectra was achieved (Table 1). The frequencies below 2000 cm^{-1} agree well without scaling.

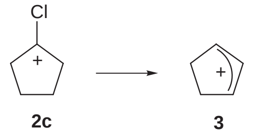
2-Propyl cations

When 2,2-dichloropropane was codeposited with an excess of SbF$_5$ on the CsI window at 77 K, only the starting material was identified in the IR spectrum. The spectrum of α-chloro substituted 2-propyl cation **1c** started to appear by warming the matrix to 240 K. The characteristic signal at 2846 cm^{-1} (Fig. 2) could be assigned to the C$_\beta$–H stretching vibration of the bond which interacts hyperconjugatively with the positive carbon atom. **1d** was prepared from 1,1,1-trichloroethane under similar conditions. By comparing the spectral data for 2-propyl cations **1a**–**1c**, it can be seen that the hyperconjugative lowering of the C$_\beta$–H stretching frequency is almost equal in **1b** (2845 cm^{-1}) as in **1c** (2846 cm^{-1}), but differs from that in **1a** (2730 cm^{-1}).[9] This result corroborates our hypothesis that both substituents, CH$_3$ and Cl, are almost equally strong electron donors.

Cyclopentyl cations

The chloro substituted cyclopentyl cation **2c** was prepared independently from two precursors, *i.e.* 1,1-dichlorocyclopentane and 1,2-dichlorocyclopentane. In both experiments, identical spectra assigned to ion **2c** were obtained (Fig. 3). Assignation of the spectrum should, whenever possible, additionally be confirmed by a preparation of the same cation from different precursors under similar experimental conditions. In that sense, we have recorded the spectrum of the chlorocyclopentyl cation starting from two different dichlorides. Also, the 7-norbornyl cation[12c] has been isolated from three different precursors. Similarly, the IR spectrum of the parent allyl cation[12d] was recorded starting from three different precursors. These are examples of isolations of carbocations which are known as being very unstable but, in spite of this, no precursor-SbF$_5$ complexes have been observed. The cation was identified by the appearance of a characteristic strong C$^+$–Cl wagging mode band at 1075 cm^{-1}. The stretching vibration of the hyperconjugatively weakened C$_\beta$–H bond was observed at 2780 cm^{-1}.

Further warming of **2c** in the matrix (above 200 K) resulted in its decomposition, which was indicated by the appearance of a new band at 1495 cm^{-1}. This indicates that **2c** eliminates HCl and rearranges to the stable cyclopentenyl cation **3**. The 1495 cm^{-1} band could tentatively be assigned to ν_{as} of the allyl group since all reported allyl cations afford a signal between 1500 and 1580 cm^{-1}.[6f,13] The same rearrangement of **2c** was previously observed by NMR in superacid medium.[14]



The C$_\beta$–H stretching frequency in the chloro ion **2c** (2780 cm^{-1}) is almost the same as in the methyl substituted ion **2b** (2765 cm^{-1}). This implies, as in the previous case, that the extent of the electron donation of CH$_3$ and Cl substituents in this cation is also of comparable magnitude.

The remarkable effect of *n*-electron back-donation on increasing the C–Cl stretching frequency was not observed in **1c**, but in **2c** an increase in frequency of the C–Cl wagging vibration (at 1075 cm^{-1}) was observed instead. In our previous work,[6g] we have shown that changes in C–Cl vibrations caused by *n*-electron back-donation differ for different α-chlorocarbocations. The calculated C–Cl bond lengths in **1c** (1.667 Å) and in **2c** (1.661 Å) are 0.04 Å shorter than a typical C(sp^3)–Cl bond distance (1.7 Å). This shortening of C–Cl bonds caused by the α-chloro effect is smaller than the value of 0.067 Å reported by Laube *et al.*[5] from X-ray single crystal measurements.

Conclusion

The lowering of C_β–H stretching frequencies in carbocations induced by hyperconjugation was tested as a possible probe for estimating the electron donating ability of α-chloro substituents. It was found that both a methyl group and chlorine as α-substituents stabilize a carbocation with almost the same effectiveness. From the spectra of various α-chloro carbocations it seems that the C–Cl stretching frequency does not always occur at frequencies as high as 1000 cm^{-1}.

Experimental

The precursors for cations **1c** and **1d**, *i.e.* 2,2-dichloropropane and 1,1,1-trichloroethane, are commercially available (Aldrich). Cation **2c** was prepared separately from two precursors, *i.e. trans*-1,2-dichlorocyclopentane and 1,1-dichlorocyclopentane. The former was prepared from cyclopentene by a previously described procedure.[15] 1,1-Dichlorocyclopentane was obtained by the reaction of cyclopentene with $SbCl_5$ in tetrachloroethane.[16]

SbF_5-matrix experiments

The samples were deposited in a liquid nitrogen cooled cryostat and/or closed cycle helium cryostat Leybold-Heraeus ROK 10-300 and the CsI cold window was held at 77 K under 10^{-5} Torr vacuum. The matrix : sample ratio was about 500 : 1. All ions were prepared by the published procedure[8a,17] from the corresponding chloride (methyl substituted) and dichloride (chloro substituted) precursors by codeposition with excess SbF_5 (1 : 500) on a CsI window cooled to 10 or 77 K respectively. Deposition times were 10–12 min. Spectra were recorded on a Perkin-Elmer 1725x FT-IR spectrometer with 2 cm^{-1} resolution.

Acknowledgements

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