Chlorocarbocations and Concept of the Electron Donating Ability*

Hrvoj Vančik

Department of Chemistry, Faculty of Science, University of Zagreb, Strossmayer trg 14, 10000 Zagreb, Croatia

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Stabilization effects and the electron donating ability of α-substituents in carbocations are considered as different chemical concepts. The discussion is based on quantum chemical and spectroscopic investigations of methyl- and chlorosubstituted carbocations. It has been demonstrated that the methyl group affords a better stabilizing effect but that chlorine acts as a better electron donor. These effects are studied in classical α-chlorocarbocations as well as in chloroallyl cations and aromatic systems.

Key words: chlorocarbocations, methylsubstituted carbocations, electron donating ability

INTRODUCTION

On the basis of systematic investigations of α-substituent effects on the stabilization of carbocations, Zuilhof et al.¹ have concluded that stabilization of a carbocation by some substituent and the electron donating ability of this substituent are two separate chemical concepts. While stabilization can be estimated by studying the thermodynamics of isodesmic reactions, electron donating ability is recognized from changes of the positive charge on the carbocation center in going from the neutral precursor to the carbocation, or from variations of bond orders. Interestingly, it was found that a methyl group affords a better stabilizing effect than chlorine, but chlorine has better electron donating properties than the methyl group.¹

* XVI Hrvatski skup kemičara i kemijskih inženjera, Split, veljača 1999.
Changes of vibrational frequencies of groups directly attached to the positive carbon atom could also be used as an indication of electron redistributions caused by the electron donating effect. In this work, we present a review of the results of our investigations of α-chlorocarbocations by quantum chemical calculations as well as by FTIR spectroscopy in solid superacid matrices, which in our opinion support the concept formulated by Zuihof et al. The discussion is focused on the comparison of chlorine and methyl group as α-substituents in carbocations. While their through σ-bond inductive effects are opposite (+I for CH₃ and −I for Cl), their »π-type« interactions with C⁺ atom are qualitatively of the same nature. Methyl group acts as an electron donor by hyperconjugation and chlorine by back donation of n-electrons (Scheme 1). This review starts with instructive examples of CH₃ and Cl effects on solvolysis rates.

![Scheme 1](image)

**DISCUSSION**

*Solvolysis of bridgehead substituted methyl- and chloroderivatives of 7-norbornyl esters.* The influence of both substituents in terms of stabilization effects on the carbocation-like transition state was previously investigated by measurements of the solvolysis rates of different methyl- or chloro-substituted derivatives.² It has been established that the methyl group stabilizes but chlorine destabilizes the carbocation-like transition state. For instance, while the methyl group enhances the solvolysis rate of 1-methyl-7-norbornyl ester 1 relative to unsubstituted 7-norbornyl derivative 2, chlorine diminishes the solvolysis rate of 1-chloro-7-norbornyl analog 3. However, it has been found that further decrease in reaction rate by two chlorine substituents, as in 1,4-dichloro-7-norbornyl ester 4, is too small to be explained only as an inductive destabilization. Consequently, the effect of chlorine on the structure of 7-norbornyl cation-like transition state is not exclusively result of inductive destabilization.² A stabilizing effect caused by chlorine n-electron back donation described by resonance forms in Scheme 2 could also be operative.

*Vibrational hyperconjugative effect.* Donation of electrons from a methyl group to the positively charged carbon can easily be explained as an interaction of a
pseudo \( \pi \)-orbital of \( \text{CH}_3 \) with the empty \( p \)-orbital on the cationic carbon atom. Such an interaction will cause a decrease in electron density in \( C_\beta -H \) bond of the \( \text{CH}_3 \) group (Scheme 3). Consequently, hyperconjugation could be recognized from lowering the \( C_\beta -H \) stretching force constant and its vibrational frequency. This down frequency shift was observed in IR spectra of simple carbocations. The largest shift of \(-200 \text{ cm}^{-1} \), relative to the average value of asymmetric \( \text{CH}_3 \) stretching frequency in saturated hydrocarbons, was observed in the spectrum of the 2-propyl cation\(^3\) where the \( C_\beta -H \) stretching absorption appears at \( 1730 \text{ cm}^{-1} \). Such a hyperconjugative frequency decrease has also been observed in partially deuterated carbocations.\(^4\) The \( C_\beta -D \) stretching frequency of the \( \text{CD}_3 \) group in 2-deuteromethyl-2-benzonorbornyl cation (5) shows up at \( 2066 \text{ cm}^{-1} \) and it is lowered by \( 158 \text{ cm}^{-1} \) relative to the corresponding precursor 6.

This possibility of accurate measuring of the hyperconjugative change in \( C_\beta -H \) stretching frequency may be applied to direct estimation of the electron donor ability of the \( \alpha \)-substituent \( R \) (Scheme 3).\(^5\)
If R acts as a good electron donor, the electron demand from the neighboring Cβ-H bond is smaller and the hyperconjugative decrease of the Cβ-H stretching frequency is diminished (i.e., Cβ-H stretching frequency is higher). Oppositely, if R is a poor electron donor, hyperconjugation of the Cβ-H bond is stronger and the lowering of the Cβ-H stretching frequency is more pronounced. The results of such an approach to the investigation of the effects of a methyl group versus the effect of chlorine have shown that both substituents (R = CH₃ or Cl) are almost equally good electron donors. The Cβ-H stretching frequencies in α-CH₃ and α-Cl substituted 2-propyl 7 and 1-cyclopentyl cations 8 (Refs. 6 and 7) have very close values (Table I). Furthermore, it seems that, to some extent, chlorine affords a better electron donating ability. The conclusion that Cl acts as a better electron donor than a CH₃ group follows also from the work of Zuilhof et al.¹ However, in contrast to this vibrational Cβ-H effect, the calculated elongation of the specifically oriented Cβ-H bond,¹ which is parallel with the empty p-orbital on C⁺ (Scheme 3), is not satisfactorily correlated with the electron donating ability of R.

α-Chloro effect. Back donation of chlorine n-electrons to the carbocation center has been observed experimentally in NMR⁸ and IR spectra⁹ of the CCl₃⁺ cation. In this ion, the C–Cl stretching frequency increases to 1040 cm⁻¹, i.e. it is 250 cm⁻¹ higher than in neutral alkyl chlorides. This could be
easily explained by a partially double bond character of the C\(^+\)–Cl bond in \(\alpha\)-chlorocarbocations (see Scheme 1). In the simpler cation, CHCl\(_2^+\), this vibration was observed at almost the same frequency (1045 cm\(^{-1}\)).\(^6\) However, the parent \(\alpha\)-chlorocarbocation CH\(_2\)Cl\(^+\) has never been isolated. In superacid medium it preferentially forms complexes (chloronium ions) with the unreacted precursor (CH\(_2\)Cl\(_2\)).

<table>
<thead>
<tr>
<th></th>
<th>hyperconjugative (\nu C^\beta-H/cm^1)</th>
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<th></th>
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<tr>
<td></td>
<td>calc.</td>
<td>calc. (\times 0.95)</td>
<td>exp.</td>
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<td>CH(_3)</td>
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<tr>
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<td>2817</td>
<td>2845</td>
</tr>
<tr>
<td>Cl</td>
<td>2981</td>
<td>2832</td>
<td>?</td>
</tr>
<tr>
<td>CH(_3) Cl</td>
<td>2901</td>
<td>2756</td>
<td>2765</td>
</tr>
<tr>
<td>Cl</td>
<td>2934</td>
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### TABLE I

Experimental and calculated (B3-LYP/6-31G(d)) C\(\beta\)–H stretching frequencies affected by hyperconjugation (see Ref. 5)
The vibrational effect of the chlorine n-electron back donation was also observed in the 2-chloro-2-norbornyl cation (9). This ion was prepared in the solid cryogenic SbF$_5$ matrix independently from three different precursors (Scheme 4). The typical C$^+$–Cl stretching frequency appeared at 1069 cm$^{-1}$.

**a-Chloro effect and aromaticity.** The simplest aromatic polychlorinated carbocation, the trichlorocyclopropenyl cation (10), has been prepared as a salt with BF$_4^-$ anion. Its geometry has been calculated by high level *ab initio* methods and determined by X-ray chrystallography. In comparison with the precursor C$_3$Cl$_4$ (11), the C–Cl bond of the cation is 0.053 Å shorter. Similar shortenings of the C–Cl bonds have been observed by X-ray diffraction methods in other α-chlorocarbocations. For instance, T. Laube's measured value is 0.067 Å. An increase in C$^+$–Cl stretching frequency in 10 has not been observed, probably due to a strong coupling between C–C and C–Cl vibrational modes.

Pentachlorocyclopentadienyl cation (12), which according to Hückel's rule should be regarded as antiaromatic, was previously characterized by e.p.r. and by FT-IR spectroscopy. By comparison of experimental and calculated IR spectra, it was concluded that the symmetry of 12 is $D_{5h}$ and the ground state is triplet. On the other hand, the tetrachloro analog 13 has $C_{2v}$ symmetry and a singlet ground state. Its structure could be regarded as composed of two substructures, 1,3-dichloroallyl cation and dichlorinated alkene. Consequently, the decrease in C–Cl bond lengths (relative to the C–Cl bondlength in chloroalkenes) is larger in the allyl cation substructure of 13 (0.040 Å) than in cation 12 (0.025 Å).
Shortening of C–Cl bonds in cyclic systems 10, 12 and 13 undoubtedly indicates the electron donating effect of the chlorine atom, in spite of the intrinsic stabilization of cations by ring π-electron delocalization. Although small, this chloro effect follows also from the calculated (Mulliken) positive charges located on Cl atoms (+0.25 in 10 and +0.317 in allyl substructure of 13) and from the enhanced C–Cl bond order in 10 (1.09, MP2/6–311G(d,p)).

However, chlorine atoms have no stabilizing effect in 10. This conclusion results from the almost negligible reaction enthalpy (3.4 kJ/mol) calculated for the isodesmic reaction represented in Scheme 5.

These examples clearly demonstrate the proposed distinction between stabilization and electron donation ability as two separate chemical concepts.

Chloroallyl cations and the stabilization of transition states. The fundamental difference in electron donating ability of chlorine in 1- (14, 15) or in 2-chloroallyl cations (16) can be explained by the different overlap of the chlorine n-electron p-orbital with LUMO of the allyl π-system. While such an overlap operates in 14 and 15, it vanishes in 16, because the LUMO atomic orbital coefficient on the central C-atom of the allyl group is zero. Consequently, the electron donating ability of chlorine was found by calculations only in 14 and 15 as a shortening of C-Cl bonds to 1.640 and 1.646 Å, respectively. Noninteraction of n-electrons with LUMO in 16 can, on the other hand, be an explanation for its possible rearrangement to the bridged chlorine ion 17 (Scheme 6). From quantum chemical calculations (MP2/6–311G**) it follows that structure 16 is 7.5 kcal/mol more stable than 17.
Electron donating ability of chlorine results also from the changes in vibrational frequencies of the asymmetric stretching of the allyl CCC+ group. While the central position of chlorine in 16 practically does not change the CCC+ stretching frequency in comparison with the parent allyl cation,20 terminal chlorines decrease this frequency to 1564 cm\(^{-1}\) and 1558 cm\(^{-1}\) in 14 and 15, respectively (Table II).21

Comparison of the methyl- versus chlorine effect on the stabilization of the transition state can be investigated by a study of cis-trans isomerization of 1-chloroallyl cations (Scheme 7). This reaction has been observed experimentally in solid SbF\(_5\) matrices.21

### TABLE II
Vibrational frequencies of asymmetric stretching of the allyl CCC+ group\(^{19}\)

<table>
<thead>
<tr>
<th>cation</th>
<th>(\nu_{\text{as}}) (CCC+) in cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="14" /></td>
<td>1564</td>
</tr>
<tr>
<td><img src="image" alt="15" /></td>
<td>1558</td>
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<tr>
<td><img src="image" alt="17" /></td>
<td>1578</td>
</tr>
</tbody>
</table>
Calculated (MP2/6–31G*) activation energy for isomerization of chloro derivatives 14 and 15 (21.1 kcal/mol) is very close to the value found for the reaction of the methyl analogs 18 and 19 (25.2 kcal/mol). In this special case, in which the activation energy depends only on π-electron redistribution, both effects, stabilization and electron donating ability, are quantitatively the same and both substituents (CH₃ and Cl) have a similar effect. Moreover, chlorine is a 4 kcal/mol better electron donor, i.e. in agreement with conclusions presented in this work.

CONCLUSIONS

1. Stabilization effect and electron donating ability are two distinct chemical concepts as suggested by Zuilhof et al. While the extent of stabilization can be calculated by a study of isodesmic and/or homodesmic reactions, the electron donating ability can be estimated on the basis of the specific geometrical changes and spectroscopic data.

2. Electron donating abilities of chlorine and a methyl group as α-substituents in carbocations are comparable, although in a series of examples chlorine acts as a better electron donor. On the other hand, the stabilization effect of methyl group is much larger.

3. In special cases (cis-trans isomerism), in which practically only the redistribution of π-electrons contributes to the energy of transition state, both effects (stabilization effect and electron donating ability) are quantitatively the same.

4. In cyclic aromatic or antiaromatic systems, chlorine shows only a small electron donating effect and does not stabilize the molecule.

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SAŽETAK

**Klorokarbokationi i koncept elektron-donirajućih sposobnosti**

*Hrvaj Vančík*

Ideja da su *stabilizacijski učinak* α-supstituenta na karbokation i *elektron-donirajuća sposobnost* tog istog supstituenta dva različita kemijska koncepta, raspravljanje na temelju rezultata kvantnokemijskih računa i spektroskopskih mjerenja. Pokazalo se da je metilna skupina bolji stabilizator karbokationa, ali da je klor učinkovitiji donor elektrona. Navedeni učinci raspravljani su na primjerima klasičnih, kloralnilnih i aromatskih α-klorokarbokationa.