Chlorocarbocations and Concept of the Electron Donating Ability*

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Stabilization effects and the *electron donating ability* of α-substit-
uents in carbocations are considered as different chemical concepts.
The discussion is based on quantum chemical and spectroscopic in-
vestigations of methyl- and chlorosubstituted carbocations. It has be-
en demonstrated that the methyl group affords a better stabilizing
effect but that chlorine acts as a better electron donor. These ef-
fects are studied in classical α-chlorocarbocations as well as in chlo-
roallyl cations and aromatic systems.

Key words: chlorocarbocations, methylsubstituted carbocations, elec-
tron 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 bet-
ter electron donating properties than the methyl group.[1]

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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 Zuilhof *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 CH_3 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 CH_3 and Cl effects on solvolysis rates.
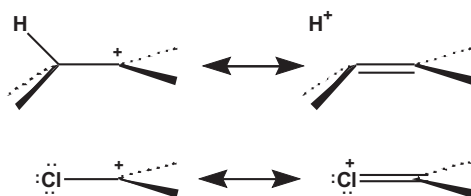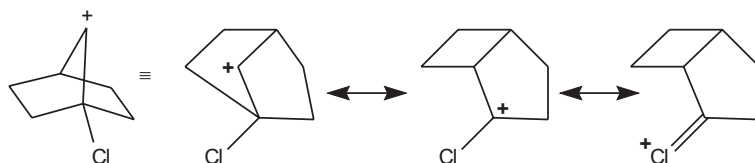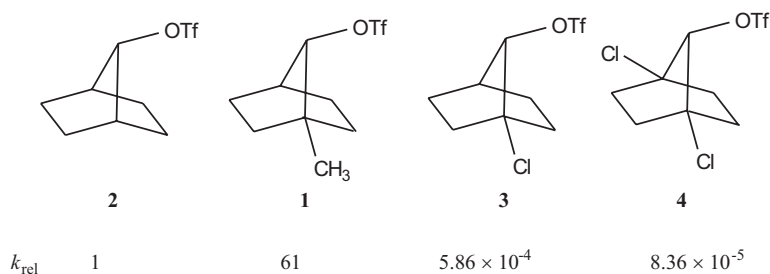

Scheme 1

DISCUSSION

Solvolysis of bridgehead substituted methyl- and chloroderivates 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
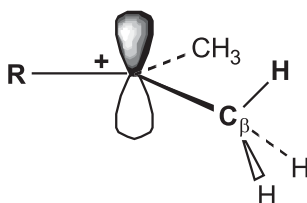
Scheme 2

pseudo π-orbital of CH_3 with the empty p-orbital on the cationic carbon atom. Such an interaction will cause a decrease in electron density in C_β-H bond of the CH_3 group (Scheme 3). Consequently, hyperconjugation could be recognized from lowering the C_β-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 cm^{-1}, relative to the average value of asymmetric CH_3 stretching frequency in saturated hydrocarbons, was observed in the spectrum of the 2-propyl cation[3] where the C_β-H stretching absorption appears at 1730 cm^{-1}. Such a hyperconjugative frequency decrease has also been observed in partially deuterated carbocations.[4] The C_β-D stretching frequency of the CD_3 group in 2-deuteromethyl-2-benzonorbornyl cation (**5**) shows up at 2066 cm^{-1} and it is lowered by 158 cm^{-1} relative to the corresponding precursor **6**.

This possibility of accurate measuring of the hyperconjugative change in C_β-H stretching frequency may be applied to direct estimation of the *electron donor ability* of the α-substituent R (Scheme 3).[5]
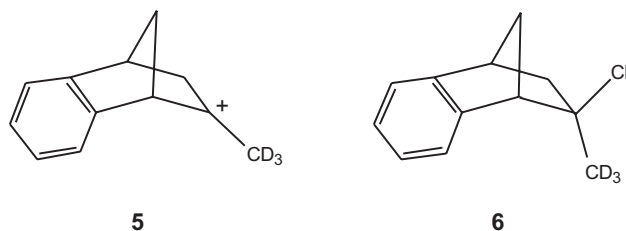
If R acts as a good electron donor, the electron demand from the neighboring C_β-H bond is smaller and the hyperconjugative decrease of the C_β-H stretching frequency is diminished (*i.e.*, C_β-H stretching frequency is hig-

Scheme 3

her). Oppositely, if R is a poor electron donor, hyperconjugation of the C_β-H bond is stronger and the lowering of the C_β-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 = CH_3 or Cl) are almost equally good electron donors. The C_β-H stretching frequencies in α-CH_3 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 CH_3 group follows also from the work of Zuilhof *et al.*[1] However, in contrast to this *vibrational* C_β-H effect, the calculated *elongation* of the specifically oriented C_β-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 NMR[8] and IR spectra[9] of the CCl_3^+ 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
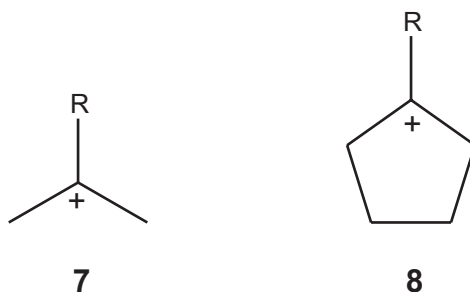

7   **8**

TABLE I

Experimental and calculated (B3-LYP/6-31G(d)) C_β–H stretching frequencies affected by hyperconjugation (see Ref. 5)
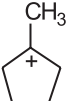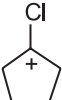
	hyperconjugative νC_β-H /cm^{-1}		
	calc.	calc. × 0.95	exp.
(CH$_3$)$_2$CH$^+$ (H)	2888	2744	2730
(CH$_3$)$_2$C$^+$–CH$_3$	2974	2825	2845
(CH$_3$)$_2$C$^+$–Cl	2965	2817	2845
CH$_3$–C$^+$(Cl)–Cl	2981	2832	?
cyclopentyl cation (H)	2857	2686	2658
cyclopentyl cation (CH$_3$)	2901	2756	2765
cyclopentyl cation (Cl)	2934	2787	2780

easily explained by a partially double bond character of the C$^+$–Cl bond in α-chlorocarbocations (see Scheme 1). In the simpler cation, CHCl$_2^+$, this vibration was observed at almost the same frequency (1045 cm^{-1}).[9] However, the parent α-chlorocarbocation CH$_2$Cl$^+$ has never been isolated. In superacid medium it preferentially forms complexes (chloronium ions) with the unreacted precursor (CH$_2$Cl$_2$).

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).[10] The typical C^+–Cl stretching frequency appeared at 1069 cm^{-1}.
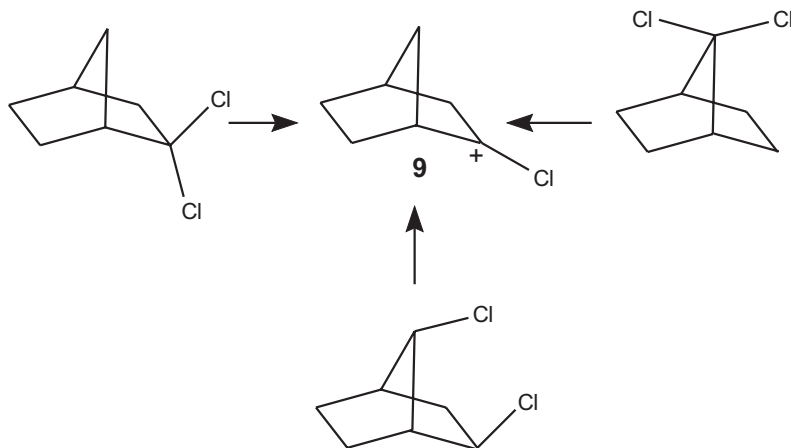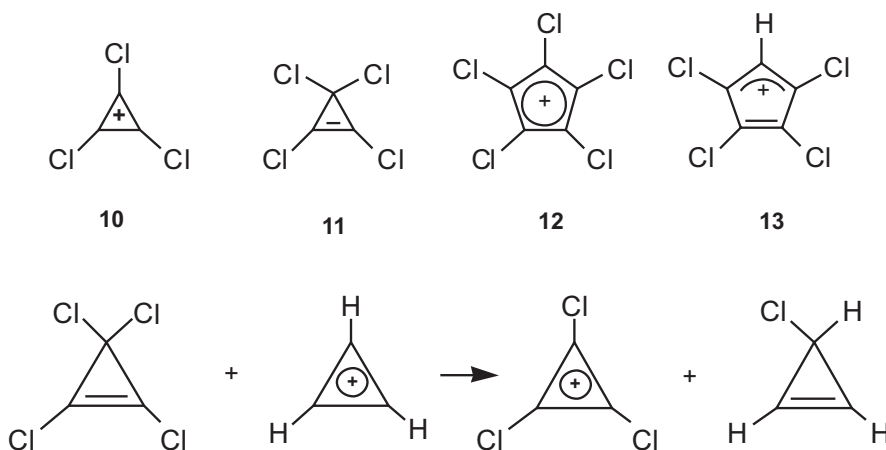

Scheme 4

α-*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.[11] In comparison with the precursor C_3Cl_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[12] 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.[13] and by FT-IR spectroscopy.[14] 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.[15] Its structure could be regarded as composed of two substructures, 1,3-dichloroallyl cation and dichlorinated alkene. Consequently, the decrease in C–Cl bond lenghts (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)).[16]

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.[17]

10   11   12   13

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).[18] From quantum chemical calculations (MP2/6–311G**) it follows that structure **16** is 7.5 kcal/mol more stable than **17**.[19]
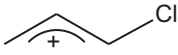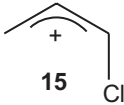
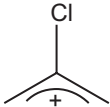**14**   **15**   **16**   **17**
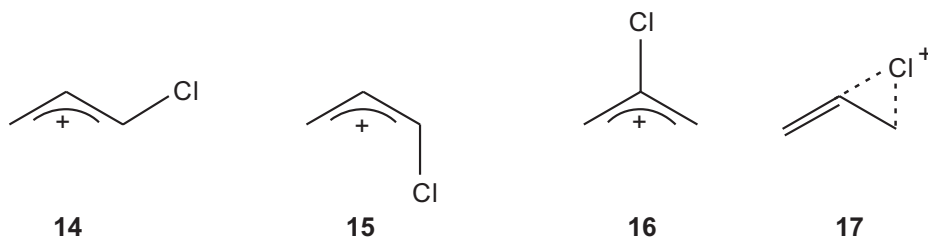
Scheme 6

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]

cation	ν_{as} (CCC+) in cm^{-1}
14	1564
15	1558
16	1574
	1578
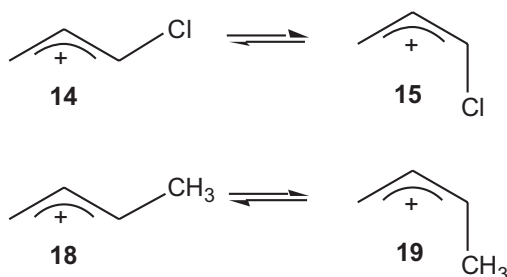
Scheme 7

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 (CH_3 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

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Ideja da su *stabilizacijski učinak* α-supstituenta na karbokation i *elektron-donirajuća sposobnost* tog istog supstituenta dva različita kemijska koncepta, raspravljana je 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, kloralilnih i aromatskih α-klorkarbokationa.