

## Matrix isolation and vibrational spectroscopy of carbocations

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**Abstract:** It is reported that some unstable species, such as cyclopropylcarbiny-, cyclooctyl-, 2-butyl- and 7-norbornyl- carbocations, can be prepared in the  $\text{SbF}_5$  matrix and investigated by IR spectroscopy combined with high level *ab initio* calculations. Direct measurements of the changes in bond strengths, i.e. changes of vibrational frequencies ( $\Delta\nu/\text{cm}^{-1}$ ) induced by forming the cationic species, could yield fundamental information on the neighboring group effects. Results of systematic investigations along these lines include studies of the complexes of nitriles and ketones with  $\text{SbF}_5$ , allyl and propargyl cations and chlorocarbocations.

### INTRODUCTION

Olah's fundamental work (1), reporting the preparation of stable carbocations in superacid media, enabled the use of a variety of spectroscopic and diffraction methods (2) for direct examination of the structure of carbocations. The main spectroscopic method used for the study of carbocations prepared in superacids was NMR because this method enables not only unequivocal determination of the structure but also investigation of their rearrangements. The possibility of exact interpretation of the NMR spectra and a relatively simple experimental method for the preparation of carbocations has until recently outshined the use of vibrational spectroscopies. In the past, only a few papers (3) were published on the IR and Raman spectra of carbocations. A more extensive use of IR spectroscopy began after the development of matrix isolation methods in which the superacid ( $\text{SbF}_5$ ) was used as matrix material. (4) At the same time, the development of quantum chemistry and computers improved our ability to interpret the vibrational spectra by comparing theoretical and experimental frequencies and intensities.

There are several important reasons for adding the use of IR spectroscopy to NMR in the study of carbocations.

Low reaction barriers often lead to extremely rapid rearrangement reactions in carbocations. At very rapid interchange rates, the NMR spectra are averaged over all the species that are being interconverted. Since the vibrational transitions are much faster, one should see separate, individual IR spectra of such rapidly interconverting species. It is also possible to obtain IR spectra at very low temperatures where many rearrangements are frozen.

In the cases where complete assignments of the IR frequencies can be made with confidence, force constants are obtained which yield important information about the change in the character of particular chemical bonds. *Changes of the characteristic group vibration frequencies* ( $\Delta\nu$ ) on going from a particular hydrocarbon or starting halide to the corresponding carbocation afford useful structural information. These second order effects ( $\Delta\nu$  values) are a very useful tool for studying the details of electronic effects operating in carbocations (e.g. conjugation, hyperconjugation, inductive effects). The relationship between  $\Delta\nu$  and some structural parameters are also helpful in cases where, even under matrix conditions, it is not possible to prepare particular ions. In such cases, complexes of ketones, nitriles and halides with strong Lewis acids, which are analogs of carbocations, have been shown to be appropriate models.

## STUDY OF POTENTIAL ENERGY SURFACES

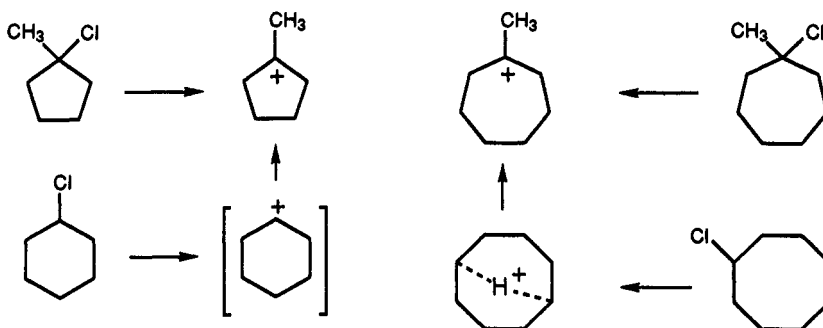
Investigations of carbocationic potential energy surfaces by means of the  $\text{SbF}_5$ -matrix IR-spectroscopy combined with high level *ab initio* calculations have elucidated some long standing problems in carbocation chemistry. The specific experimental conditions enabled isolation of several elusive cations for the first time.

Rearrangements of  $\text{C}_4\text{H}_9^+$  isomers that lead to t-butyl cation were investigated by studying the ionization of 2-chlorobutane in the  $\text{SbF}_5$  matrix. (5) The first intermediate characterized after the ionization was the 2-butyl cation. Its H-bridged structure and the corresponding IR spectrum with the characteristic signal of the  $\text{C}-\text{H}^+-\text{C}$  stretching vibration at  $2175\text{ cm}^{-1}$  was predicted also by *ab initio* calculations. (6) This ion was observed at  $-60\text{ }^\circ\text{C}$ , while further warming of the matrix to  $-10\text{ }^\circ\text{C}$  led to the most stable isomer, the tert-butyl cation (Scheme 1). The spectrum of t-butyl cation was assigned by comparison with the spectrum obtained by direct ionization of tert-butyl chloride. (5,1)



Scheme 1

Upon ionization in superacid medium, cyclohexyl chloride rearranges to the 1-methylcyclopentyl cation (Scheme 2). (7) The IR spectrum recorded after warming the  $\text{SbF}_5$ -matrix isolated cyclohexyl chloride to  $-110\text{ }^\circ\text{C}$  was identical with the spectrum obtained by ionization of 1-chloro-1-methylcyclopentane. (4c) Thus, both spectra were assigned to the 1-methylcyclopentyl cation. However, the isolation of the intermediate cyclohexyl cation failed, and consequently the detailed mechanism of this rearrangement remains insufficiently explained.



Scheme 2

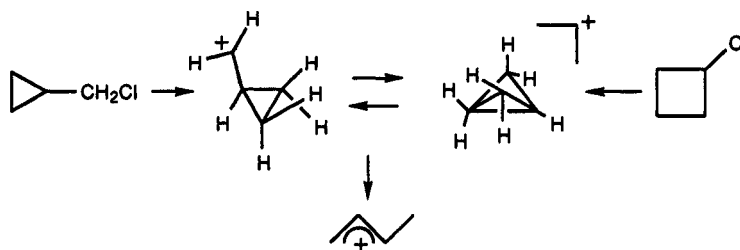
Scheme 3

A similar ring contraction occurs on ionization of cyclooctyl chloride (Scheme 3). (8) However, a stabilization of cyclooctyl cation by transannular H-bridging (9) enabled its isolation in the  $\text{SbF}_5$  matrix. The appearance and vanishing of the cyclooctyl cation was followed by viewing the characteristic absorption at  $1845\text{ cm}^{-1}$  assigned to the  $\text{C}-\text{H}^+-\text{C}$  stretching vibration. (10) The spectrum of cyclooctyl cation was recorded at a very low temperature ( $-165\text{ }^\circ\text{C}$ ) because above  $-110\text{ }^\circ\text{C}$  the ion rearranges to 1-methylcycloheptyl cation. This final tertiary cation (Scheme 3) was also independently prepared from 1-chloro-1-methylcycloheptane.

Two longstanding problems, the structures and rearrangements of cyclopropylcarbanyl (11) and 7-norbornyl cation, (12) were also studied in detail by  $\text{SbF}_5$  matrix IR spectroscopy.

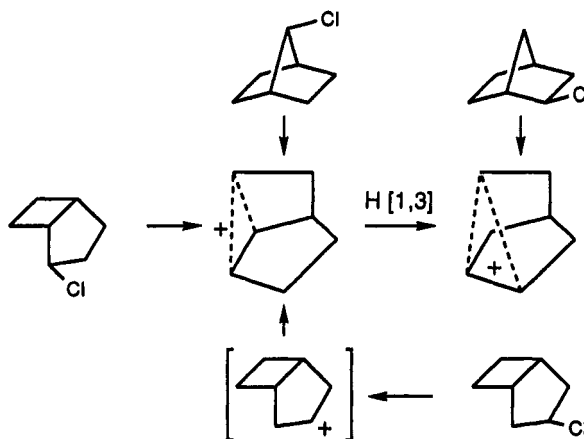
Identical spectra were recorded after either cyclopropylcarbanyl- or cyclobutyl chloride had been ionized by  $\text{SbF}_5$ . (13) The best agreement of these spectra was found with the *ab initio* (MP2/6-31G\*) computed frequencies for a combination of frequencies for the bicyclobutonium ion and the cyclopropylcarbanyl cation by assuming that both isomers (Scheme 4) are present in the reaction

mixture (matrix). This evidence, that the cations are rapidly equilibrating non-classical structures, additionally supports the structures previously proposed on the basis of the CP MAS (14) experiments and the calculated IGLO (15) chemical shifts. Rearrangement of both cations to methylallyl cation (Scheme 4) was observed by warming the matrices to 230 K.



Scheme 4

In contrast to the cyclopropylcarbanyl problem, which was successfully investigated by NMR, 7-norbornyl cation could be isolated as a long-lived species only by means of the  $\text{SbF}_5$  matrix method. (16) The characterization and structure determination of the 7-norbornyl cation added a very important point on the  $\text{C}_7\text{H}_{11}^+$  hypersurface. The calculated IR spectrum, which agrees well with the experimental one, corresponds to the nonclassical structure of the 7-norbornyl cation. This ion was prepared from three different precursors, 7-chloronorbornane, 2-chlorobicyclo[3.2.0]heptane and 3-chlorobicyclo[3.2.0]heptane (Scheme 5). (17) In all these experiments, a rearrangement to the most stable 2-norbornyl cation was observed (Scheme 5). On the basis of *ab initio* calculations, it was concluded that the barrier for the rearrangement of 7- to 2-norbornyl cation is relatively high (65 kJ/mol). (16) This is the main reason why the ion could be isolated in spite of its relative instability.



Scheme 5

#### APPLICATION OF SECOND ORDER ( $\Delta\nu$ ) EFFECTS

**Carbocations.** - A change in the stretching frequency,  $\Delta\nu$ , can be an excellent measure for the estimation of the weakening or strengthening of a specific chemical bond if the positive charge appears in the vicinity.

Weakening of carbon-carbon multiple bonds can *inter alia* be caused by conjugative delocalization. In allyl cations (13) a decrease in the  $\text{C}=\text{C}$  stretching frequency has been found. The typical position of the allylic  $\text{C}=\text{C}=\text{C}^+$  stretching signal below  $1600\text{ cm}^{-1}$  helped us to characterize even the parent allyl cation, recently prepared in the solid  $\text{SbF}_5$  matrix. (18)

A frequency shift to lower wavenumbers was also found for the propargyl cations. (19a) A comparison of  $\Delta\nu$  ( $\text{C}\equiv\text{C}$ ) values for the differently substituted propargyl cations can also provide information about the electron donating ability of groups bound to the  $\gamma$  carbon:

	$\text{CH}_3\text{-C}\equiv\text{C-C}^+\text{R}_2$	$\text{H-C}\equiv\text{C-C}^+\text{R}_2$	$(\text{CH}_3)_3\text{Si-C}\equiv\text{C-C}^+\text{R}_2$
$\Delta\nu$	$66\text{ cm}^{-1}$	$37\text{ cm}^{-1}$	$55\text{ cm}^{-1}$

From these  $\Delta\nu$  values it follows that the  $\text{CH}_3$  group is the best electron donor and hydrogen the poorest. The trimethylsilyl group is in the middle, exactly as it was found independently on the basis of solvolysis studies. (19b,c,d)

The change of the C-H stretching frequency of the  $\beta\text{C-H}$  bond in carbocations can be associated with the hyperconjugative donation of electrons (Table 1a). While smaller frequency shifts ( $\Delta\nu \sim -220\text{ cm}^{-1}$ ) were found for the CH hyperconjugation in cyclopentyl and cumyl cations, the large shifts  $\Delta\nu > -800\text{ cm}^{-1}$ , observed in 2-butyl and cyclooctyl cations were explained by hydrogen bridging .

The electron donating abilities of  $\alpha$ -substituents R in differently substituted 2-propyl cations (Table 1b) cannot be estimated by measuring the  $\nu(\text{CH}_3)$  values. However, the  $\Delta\nu$  values, which originate from C-H hyperconjugation, are a sensitive probe for the R-group effect. Interestingly, from the data given in Table 1b it follows that the two effects, the conjugation of chlorine n-electrons and the C-H hyperconjugation of the methyl group, are very close in magnitude.

TABLE 1. Stretching frequencies (in  $\text{cm}^{-1}$ ) of the weakened C-H bond in carbocations

a)	cumylium	methylocyclopentylum	2-butylium	cyclooctylum
	2700	2755	2175	1845

b)	$\nu\text{CH}_3\text{ str /cm}^{-1}$		$\Delta\nu / \text{cm}^{-1}$
R	starting chloride	cation	
H	2965	2730	235
Cl	2999	2851	148
$\text{CH}_3$	2985	2840	145

A substantial bond strengthening ( $\Delta\nu > 0$ ) was found for the C-Cl bond in chlorocarbocations. In the trichloromethyl cation (20) the C-Cl stretching frequency is  $1040\text{ cm}^{-1}$ , i.e. higher by  $250\text{ cm}^{-1}$  than a normal C-Cl stretching frequency in saturated organic halides. The relatively high frequency of this partially double C-Cl bond is a consequence of back donation of nonbonding electrons from chlorine to the positive carbon. (21) Similar spectral characteristics were also found in the spectra of dichloromethyl- ( $1045\text{ cm}^{-1}$ ) and 2-chloro-2-norbornyl cations. (22) Interestingly, this high frequency vibration of the C-Cl bond was not found in the spectrum of trichlorocyclopropenium cation (Scheme 6). (23) Probably, the aromaticity of the three-membered cyclopropenium ring diminishes the requirement for  $n$ -electrons from the chlorine atom. In contrast, the band at  $1042\text{ cm}^{-1}$ , tentatively assigned to a C-Cl stretching vibration, appears in the IR spectrum of pentachlorocyclopentadienyl cation (Scheme 6). (24) This antiaromatic five-membered ring requires for its stabilization  $n$ -electrons from the neighboring chlorine atoms. Thus, the appearance of the large positive  $\Delta\nu(\text{C-Cl})$  can in this case be used as a criterion of aromaticity!

Scheme 6



**Complexes of Ketones and Nitriles with  $\text{SbF}_5$ . Carbocation-like Structures.** - Ketones have in many cases been found to be suitable models for  $\text{sp}^2$  hybridized carbocations. (25) It has been shown (26) that electronic interactions commonly observed in carbocations can also be observed in ketones if they are complexed with  $\text{SbF}_5$  or  $\text{BF}_3$ , which increase the polarization and hence the carbocationic character of the carbonyl group. The  $\Delta\nu$  C=O value, measured as the difference in the carbonyl stretching frequency of starting and complexed ketones, is correlated with the number  $N$  which corresponds to the number of  $\alpha$ - $\beta$  C-C bonds in the examined ketones. A good linear correlation was found (27) for the ketones that are analogs of carbocations in which inductive effects are operative. However, ketone analogs of the carbocations stabilized by bridging or hyperconjugation have a large  $\Delta\nu$  value; they are above the line. Consequently, hyperconjugation or bridging in a particular carbocation can be estimated by the  $\Delta\nu$  value of the corresponding ketone analog. There is, however, another important point. If  $\nu(\text{C}=\text{O})$  is used instead of the  $\Delta\nu(\text{C}=\text{O})$  value, no correlation with the number  $N$  was found. This is an excellent demonstration of the importance of the second order vibrational effect  $\Delta\nu$ .

In contrast to ketone- $\text{SbF}_5$  complexes, complexing of nitriles with  $\text{SbF}_5$  exhibits a positive  $\Delta\nu$  value. (28) In solid  $\text{SbF}_5$  matrices,  $\nu(\text{C}\equiv\text{N})_{\text{str.}}$  increases by  $40\text{ cm}^{-1}$  or more if *end-on coordinated* complexes (complexes in which nitrogen n-electrons are involved) are formed. Interaction of this activated nitrile group with the  $\sigma$  and/or  $\pi$ -electron system of a nitrile molecule can be estimated by analyzing the vibrational changes of its hydrocarbon skeleton. While the increased polarization of the carbonyl group, obtained by complexing of ketones with a strong Lewis acid, can be directly measured as  $\Delta\nu(\text{C}=\text{O})$ , because  $\Delta\nu(\text{C}=\text{O}) < 0$ , the increased polarization of the nitrile group (for which  $\Delta\nu(\text{C}\equiv\text{N}) > 0$ ) in similar complexes can be observed only indirectly, by measuring the  $\Delta\nu$  values of the vibrations in the rest of the nitrile molecule. For instance, the polarization of the nitrile group in acrylonitrile was uncovered because a decrease in the C=C stretching frequency from  $1605\text{ cm}^{-1}$  in the precursor molecule to  $1592\text{ cm}^{-1}$  in the  $\text{SbF}_5$  complex was observed. (29) The *side-on coordinated* complexing of nitriles with strong Lewis acids (in which  $\pi$ -electrons are involved) exhibits the "normal" frequency shift of  $\nu(\text{C}\equiv\text{N})_{\text{str.}}$  ( $\Delta\nu < 0$ ), i.e. analogously to ketone-complexes.

The frequency shifts observed by complexing of electron rich functional groups with strong Lewis acids can be qualitatively compared with the changes in vibrational frequencies measured in the fine structure of photoelectron spectra (Table 2). In both cases, it is possible to identify the particular

TABLE 2. Changes in the stretching frequencies of the carbon-heteroatom multiple bonds obtained by photoionization (PES) and by complexing with strong Lewis acids.

orbital	$\Delta\nu / \text{cm}^{-1}$		
	PES	complexing	coordination
$>\text{C}=\text{O}$ n	-184 <sup>a</sup>	-120 <sup>b</sup>	end-on
$\text{C}\equiv\text{N}$ $\pi$	-257 <sup>c</sup>	-220 <sup>d</sup>	side-on
$\text{C}\equiv\text{N}$ n	-47 <sup>c</sup>	+100 <sup>e</sup>	end-on

a) measured for  $\text{CH}_3\text{CHO}$  (Ref. 30); b) measured for acetone (Ref. 27);

c) in photoelectron spectrum (PES) of HCN (Ref. 33); d) from Ref. 2.;

e) from HCN-HBr complex (Ref. 32).

orbital from which an electron is ejected by photoionization or withdrawn by complexing. Ionization of carbonyl compounds by removal of an electron from the oxygen  $n$ -orbital (30) decreases the C=O stretching frequency by  $180\text{ cm}^{-1}$ . Similarly, the complexing of ketones with strong Lewis acids (27) affords a decrease of this frequency by  $120 - 220\text{ cm}^{-1}$  (Table 2). Analogy can be found in the comparison of the C $\equiv$ N stretching frequency shift in a side-on coordinated adduct of nitrile ( $\Delta\nu = -220\text{ cm}^{-1}$ ) with a large reduction of this frequency in the first band systems of the photoelectron spectra of nitriles ( $\Delta\nu = -257\text{ cm}^{-1}$ ). Even a very simple molecule like  $\text{N}_2$  experiences a decrease in the stretching frequency by  $153\text{ cm}^{-1}$  in the ionic  $\text{N}_2^+$  state (31) and by  $-82$  or  $-42\text{ cm}^{-1}$  in the protonated form  $\text{N}_2\text{H}^+$ , as calculated by HF/6-31G\* and MP2/6-31G\*, respectively.

The increase in the C $\equiv$ N stretching frequency ( $\Delta\nu = +100\text{ cm}^{-1}$ ) obtained by end-on coordination of HCN with  $\text{BBr}_3$  (32) is not followed by the corresponding frequency increase induced by the photoionization of electrons from the  $n$  orbital of HCN. Instead, a negligible decrease of  $\nu_{\text{CN}}$  by  $40 \pm 30\text{ cm}^{-1}$  was observed. However, this decrease is substantially smaller than the PES  $\Delta\nu$  values of other precursors (Table 2). An explanation of these observations requires more theoretical and experimental work, which is in progress in our laboratory.

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