

# In Situ X-ray Photoelectron Spectroscopic Studies of Carbocations

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**Abstract:** A method is presented for the preparation of carbocation samples in the source of an ESCA spectrometer. Comparison is made between the ionization of organic halides by antimony pentafluoride and the protonation of alkenes by fluorosulfonic acid as viable preparative routes for this purpose. Ionization of *tert*-butyl chloride showed that the C 1s internal shift of a localized tertiary carbocation is  $\geq 3.1$  eV. The C 1s core-hole spectra, obtained by protonation of norbornene and *cis*-but-2-ene, are discussed in terms of various theoretical models, and it is concluded that, under stable ion conditions, the 2-norbornyl cation has a nonclassical structure and the *sec*-butyl cation is substantially methyl bridged.

It has long been realized that X-ray photoelectron spectroscopy (XPS or ESCA)<sup>1,2</sup> is an ideal spectroscopic tool for the study of carbocations since the lifetime of a C 1s core-hole state is short ( $\sim 10^{-14}$  s) compared with the time scale of nuclear motion ( $\sim 10^{-13}$  s)<sup>3,4</sup> and because ESCA chemical shift can be calculated comparatively easily. However, the experiment is very difficult; results already obtained<sup>5-8</sup> have not gained general acceptance,<sup>9,10</sup> and it has been stated, with reference particularly to the norbornyl (bicyclo[2.2.1]heptyl) system, that it is regrettable that an independent confirmation has not been presented.<sup>10,11</sup> We report the results of some recent work aimed at developing a method that is suitable for the spectroscopic observation of interesting and controversial carbocationic systems, following their preparation in the source of an ESCA spectrometer.

It is perhaps worth stating at the start that the ESCA data belong firmly alongside the other results pertaining to studies of cations under stable ion conditions, and controversy surrounds attempts to extrapolate such results to different conditions.<sup>11-15</sup> The question that spectroscopic structural studies may be able to answer is whether nonclassical ions exist. For the 2-norbornyl cation the results from solid-state NMR experiments at 5 K<sup>16</sup> and application of the methods of isotopic perturbation of resonance<sup>17</sup> and total chemical shift difference<sup>18</sup> already indicate that the answer is in the affirmative.

In the case of the 2-butyl cation, there is as yet no overall agreement over the structure, despite its inherent simplicity. The <sup>13</sup>C NMR solution spectrum showed only two resonances,<sup>19</sup> and since it could not be assigned as derived from one ion, it was concluded that the slow time scale of the NMR experiment led to a time-averaged spectrum resulting from equilibrium between the hydrogen-bridged and degenerate classical ions. Such a conclusion requires the assumption that these ions are of similar thermodynamic stability; in light of more recent calculations, which show that with inclusion of electron correlation the H-bridged ion is some 8-10 kcal/mol more stable,<sup>20</sup> the conclusion appears to be invalid. The isotopic perturbation of resonance method, which has proved to be so diagnostic of single- and double-minima potential energy surfaces, applied to the *sec*-butyl cation, gives an intermediate splitting value of 11 ppm<sup>21</sup> (cf.: norbornyl, <2 ppm; 1,2-dimethylcyclopentyl, >100 ppm). Similarly, the total chemical shift difference between the *sec*-butyl cation and butane has a value of 309 ppm<sup>18</sup> (cf.: norbornyl, 175 ppm; 2-propyl, 376 ppm), showing it to be borderline in classical-nonclassical behavior. Solid-state <sup>13</sup>C CPMAS NMR of the *sec*-butyl cation at  $\sim 190$  K<sup>22</sup> again showed two resonances with shifts that were in good agreement with the results from solution studies. However, even on cooling to 50 K,<sup>23</sup> no further distinction was possible. Theoretical investigations have concerned five possible structures: the C<sub>1</sub><sup>24</sup> and C<sub>3</sub><sup>20,24,25</sup> open-chain conformations, the H-bridged

*trans*-but-2-ene,<sup>20</sup> the corner-protonated methylcyclopropane (fully methyl bridged),<sup>25</sup> and the partially methyl-bridged structure.<sup>25</sup> The calculated ground-state energies suggest, on the basis admittedly of incomplete geometry optimization, that the lowest energy conformation may well be the partially bridged structure. Of great importance to the present work, however, are the core-hole state spectra, which have been calculated for three of the structures<sup>25</sup> (C<sub>3</sub>, fully and partially methyl bridged), with a fourth being inferred from earlier results (H-bridged). More recently, the SCF STO-4.31G core-hole spectra have been computed<sup>26</sup> for the H-bridged<sup>27</sup> and C<sub>1</sub><sup>28</sup> forms. The latter is found

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to be essentially a 1:2:1 spectrum with internal shifts of 4.7, 1.0, and 0.8 eV ( $C_2$ ,  $C_1$ ,  $C_3$ ), from the lowest binding energy component ( $C_4$ ); this is similar to that computed for the  $C_3$  cation, though notably the internal shifts are reduced compared with those found for the  $C_3$  form (6.1, 2.1 eV). The H-bridged structure gives rise to a C 1s spectrum involving two different carbon environments of equal intensity and internal shift of 2.8 eV. From these results, it is clear that because of the enhancement of weak interactions in going to a core-ionized state, the experimental C 1s spectrum of the *sec*-butyl cation would be entirely diagnostic of its structure.

### Experimental Section

The method is based on the molecular beam technique proposed by Saunders.<sup>29,30</sup> Essentially, a grease-free vacuum line pumped by two two-state rotary pumps, an 80 L s<sup>-1</sup> E203D oil diffusion pump and liquid-nitrogen trap was interfaced to an AEI ES200B spectrometer. Two 70-mm copper gasket conflat ports on the front of the spectrometer were used to mount 6.25-mm-o.d. stainless-steel pipes with an internal length of ~8 cm; this was calculated from instrument drawings to take the molecular beams to within 2 cm of the substrate. Externally, the pipes were terminated by metal valves which, while allowing some control of the reagent beams, primarily afforded them an "on-off" capability. Originally, the organic halide was controlled by use of a capillary tube (40 × 0.5 mm), but this was soon replaced by a needle valve to permit accurate and reproducible beam conditions. The reagent flow could be further controlled by variation of bath temperatures. The pressure in the vacuum line was measured by Penning and corrosion-resistant Pirani gauges and in the spectrometer by an Ion 7 ionization gauge. Typically, the base pressures in the vacuum line and spectrometer were ~1 × 10<sup>-4</sup> and ~1 × 10<sup>-7</sup> T, respectively. To reduce antimony contamination of cooled samples, the spectrometer source was sputter-cleaned by an argon glow discharge prior to a conventional bake-out. The discharge, operated at a pressure of ~0.1 T with a current of ~9 mA for 6–8 h, was initiated with an argon ion gun of CEGB design.<sup>31</sup>

Antimony pentafluoride (Ozark Mahoning) or fluorosulfonic acid (BDH) was transferred to a Schlenk tube under an atmosphere of nitrogen. *tert*-Butyl chloride (BDH) was vacuum distilled from a tube containing phosphorus pentoxide. *exo*-2-Norbornyl chloride was prepared by the hydrochlorination of norbornene<sup>32</sup> (Aldrich); GLC and GC-MS showed that it was ~95% pure, the main impurity being unreacted norbornene, which proved difficult to separate. Prior to use, these reagents were degassed by a series of freeze-thaw cycles.

With the vacuum line and spectrometer at their base pressures, the interfacing valves were opened, and the gold substrate (22 × 6 × 0.3 mm; Johnson Matthey 99.9%) was then cooled, usually to -120 °C, by a flow of liquid nitrogen. In the experiments with *tert*-butyl chloride and antimony pentafluoride, a variety of codepositions and sequential depositions were tried, while those with norbornyl chloride, norbornene, and *cis*-but-2-ene (BDH) were all sequential depositions. In the codepositions, the first reagent was allowed to flow into the source until the desired pressure was registered by the Ion 7 source gauge, and then the second was introduced; the times noted refer to that length of time when both reagents were flowing into the source. Typically, when the beams were closed off, the pressure fell to ~4 × 10<sup>-7</sup> T within a few minutes; when the highest pressure of ~6 × 10<sup>-4</sup> T was used, this took 10–15 min. Spectral observation was usually commenced when the pressure had fallen to ~1 × 10<sup>-6</sup> T. In the sequential depositions the antimony pentafluoride or fluorosulfonic acid was deposited first. Characteristic core-level spectra confirmed the deposition and established the purity of the surface, prior to deposition of the organic species. During deposition, the substrate was normal to the molecular beams and the probe had simply to be rotated through 120° to change from the deposition to the analysis position. Curve fitting was performed with Gaussian peak shapes generated on a Du Pont 310 Analog Curve Resolver.

### Results

(a) **With *tert*-Butyl Chloride.** Antimony pentafluoride was introduced into the source until the Ion 7 gauge registered a pressure of ~2 × 10<sup>-5</sup> T, and then *tert*-butyl chloride was in-

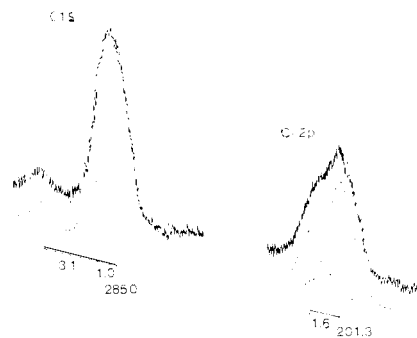


Figure 1. Core-hole spectra of a localized carbocation system. Binding energies are referenced to C 1s at 285.0, and internal shifts are in eV.

roduced to a total pressure of ~6 × 10<sup>-4</sup> T. The beams were left for ~3 min. The first C 1s and Cl 2p spectra recorded are shown in Figure 1.

The higher binding energy component of the C 1s core-hole spectrum, which is better resolved than that previously reported for the *tert*-butyl cation,<sup>5</sup> is ~10% of the total signal intensity and has a binding energy ~4.1 eV higher than the main component. The Cl 2p spectrum can be adequately represented as a single 2p<sub>1/2,3/2</sub> spin-orbit doublet. From these two spectra the C/Cl stoichiometry (determined by a standard instrumental sensitivity factor<sup>33</sup> and assuming vertical homogeneity) is ~3. A second C 1s spectrum recorded immediately after the Cl 2p spectrum (~10 min after the first C 1s) already showed some degradation, leading to a comparative loss in intensity of the higher binding energy component and broadening of the other. The C/Cl stoichiometry determined from the chlorine spectrum and the second carbon spectrum was ~2.5. The essential two-component nature of the C 1s spectrum was reproducible, but the narrow line half-width, leading to clear resolution of the peaks, proved not to be reproducible.

Experiments in which deposition was attempted at a lower total source pressure generally led to Lewis acid surfaces containing only small amounts of the alkyl halide and no evidence for an ionized system. Attempts to deposit the alkyl halide using a partial pressure of the organic halide approximately equal to that of the Lewis acid (~2 × 10<sup>-5</sup> T) but maintaining the same total pressure (~6 × 10<sup>-4</sup> T) by using a flow of helium were also unsuccessful. An alternative concentric molecular beam arrangement similar to that described by Yannoni<sup>22</sup> did not affect the results obtained.

After consecutive deposition of *tert*-butyl chloride on top of a layer of antimony pentafluoride at -120 °C, some broadening of the C 1s peak was observed over a period of ~30 min, but this experiment showed only a high binding energy tail of the primary peak rather than a second discrete peak. Allowing the system to warm to -100 °C and subsequently to -80 °C in attempts to induce ionization led mainly to the "pumping-off" of the organic system because of the high-vacuum conditions. Preparation of a more intimate mix, as a "multilayer sandwich", with a surface layer of Lewis acid did not permit the observation of organic species until the system was allowed to warm to ~+15 °C. At this temperature, the C 1s spectrum showed a broad high binding energy tail with a distinct component at 4–5 eV from the main peak; the F 1s spectrum showed a pronounced high binding energy shoulder consistent with the presence of organic fluorine on the surface, and the C/Cl ratio was ~13, again assuming bulk sensitivity factors.

(b) **With Norbornyl Chloride.** Norbornyl chloride was introduced into the source chamber until the pressure gauge registered ~1 × 10<sup>-5</sup> T and the flow allowed to continue for 1 min. A wide-scan spectrum confirmed deposition of the material onto a gold substrate precooled to -120 °C. When a standard instrumental sensitivity factor was used, high-resolution C 1s and Cl 2p core-level spectra gave a C/Cl stoichiometry of ~6.5. The

(27) E. M. Arnett's geometry from Carnegie Mellon Quantum Chemistry Archive, 1981.

(28) STO-4.31G optimized geometry from P. v. R. Schleyer.

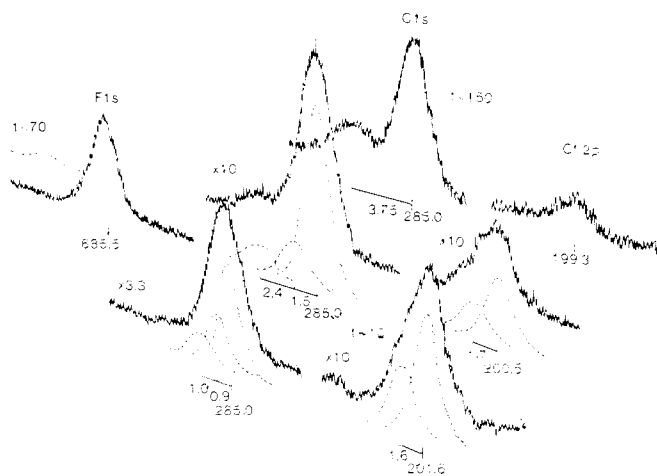
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**Figure 2.** Norbornyl chloride deposited on top of antimony pentafluoride—change of core-hole spectra with time (min) from deposition of the chloride: (A)  $t \sim 10$ ; (B)  $t \sim 70$ ; (C)  $t \sim 150$ . Binding energies are referenced to C at 285.0, and internal shifts are in electronvolts.

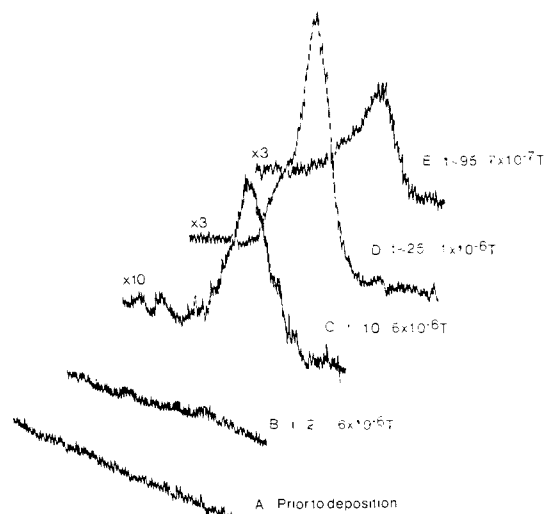
C 1s spectrum was well represented by three Gaussian components of relative intensity 4/2/1 and internal shifts of 0.4 and 1.7 eV, with the most intense component being at lowest binding energy.

A layer of antimony pentafluoride, deposited onto a substrate at  $-120^\circ\text{C}$  ( $\sim 1 \times 10^{-5}$  T, 30 s), was characterized, and in particular, the surface was observed to be relatively free of contaminant carbon species. Norbornyl chloride was introduced ( $\sim 1 \times 10^{-5}$  T, 6 s), and the carbon and chlorine spectra were recorded immediately afterward (Figure 2A). Fitting of the carbon spectrum by three peaks of intensity ratio 4/2/1 gave internal shifts of  $\sim 0.9$  and  $\sim 1.9$  eV. The C/Cl stoichiometry was  $\sim 6.4$  (assuming vertical homogeneity and bulk sensitivity factors). Approximately 30 min after the deposition of norbornyl chloride, a low-intensity peak was observed  $\sim 4$  eV from the main C 1s peak but not completely resolved from it. Over the following 40 min, this peak was seen to grow in intensity but never appeared completely resolved (Figure 2B). The minimum number of peaks required in the resolution of the C 1s spectrum is 3; these have a relative intensity of 9/2/1, and the internal shifts are  $\sim 1.5$  and  $\sim 3.9$  eV to higher binding energy of the main component. The C/Cl stoichiometry is  $\sim 6.8$ . About 80 min after deposition of the chloride, the sample was allowed to warm to  $-100^\circ\text{C}$ . Initially, there was little change in the carbon spectrum, but over a further 10 min, the high binding energy peak showed a relative increase in intensity until in the final carbon spectrum recorded (Figure 2C) it represented  $\sim 25\%$  of the total C 1s signal intensity. The final C/Cl stoichiometry is  $\sim 23$ .

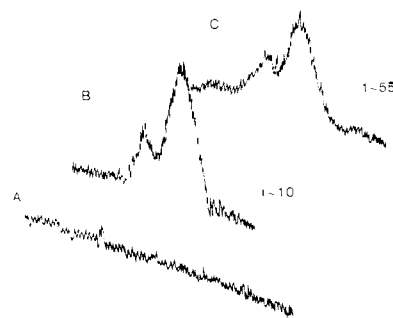
**(c) With Norbornene.** With a substrate precooled to  $-120^\circ\text{C}$ , deposition of norbornene could not be achieved. It was necessary to further cool the substrate to  $-160^\circ\text{C}$ , when deposition was obtained after the olefin was allowed in to a pressure of  $\sim 1 \times 10^{-4}$  T for 1 min. As expected, the C 1s spectrum was a single component.

Fluorosulfonic acid was introduced into the source containing a substrate at  $-120^\circ\text{C}$ , at a pressure of  $\sim 1 \times 10^{-4}$  T for 2 min. Deposition was confirmed by a single wide scan; the high-resolution C 1s core-level spectrum was observed to determine the extent of adventitious hydrocarbon surface contamination. Norbornene was then introduced ( $\sim 1 \times 10^{-4}$  T, 10 s). Initially, no deposition/reaction appeared to have occurred, but as the source pressure dropped over a period of 30 min, the carbon signal grew in intensity and developed a shoulder (Figure 3). This spectrum (3) was stable over about 15 min, with two consecutively recorded carbon spectra being identical. After this, there was a gradual decrease of intensity followed by a loss of resolution, leading to the final carbon spectrum about 90 min after the introduction of norbornene and 120 min after deposition of the acid bed. A repeat of this experiment yielded similar spectra.

**(d) With Butene.** It was not possible to deposit *cis*-but-2-ene on a substrate cooled to  $-150^\circ\text{C}$ , and even at  $-165^\circ\text{C}$  ( $\sim 6 \times$



**Figure 3.** Growth of C 1s intensity following introduction of norbornene into the source. Times (min) from introduction of the alkene—approximately 30 min after introduction of the fluorosulfonic acid bed. Source pressures are given in Torr.



**Figure 4.** *cis*-But-2-ene with a fluorosulfonic acid bed—change of C 1s spectrum with time [time (min) from inlet of alkene—approximately 30 min after inlet of acid]: (A) prior to inlet of alkene; (B) immediately after alkene inlet.

$10^{-4}$  T, 1 min), only minimal deposition was achieved.

Fluorosulfonic acid was allowed into the source ( $\sim 1 \times 10^{-4}$  T, 1 min). Deposition onto the substrate held at  $-120^\circ\text{C}$  was confirmed, and the C 1s region of the spectrum was scanned (Figure 4A). *cis*-But-2-ene was introduced ( $\sim 1 \times 10^{-4}$  T, 15 s); the source pressure was  $< 1 \times 10^{-6}$  T before the alkene was introduced and rapidly returned to this when the reagent flow was stopped. The C 1s spectrum was recorded immediately (Figure 4B) and is thus within a few minutes of the alkene introduction and within about 30 min of the acid deposition. About 30 min after the introduction of the alkene, the carbon spectrum began to change, showing in particular the growth of an even higher binding energy peak (Figure 4C). In further experiments, the inlet conditions of the alkene were varied from  $\sim 1 \times 10^{-5}$  to  $\sim 1 \times 10^{-4}$  T, but essentially the same C 1s spectrum was observed in each case.

## Discussion

The C 1s spectrum of the *tert*-butyl cation has been experimentally determined to be two components with a C 1s internal shift (C 1s[C<sup>+</sup>]-C 1s[C-C<sup>+</sup>]) of 3.9 eV.<sup>7</sup> The shift has been theoretically calculated (at the SCF STO-4.31G level) as 3.8 eV.<sup>34</sup> For a pure cation sample, the two components are expected to exhibit a 3/1 intensity ratio with the peaks corresponding to the methyl carbons and the cation center itself. Obviously, therefore, while the internal shift of the two components of the C 1s spectrum, shown in Figure 1, is consistent with a localized carbocation,

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the intensity ratio (9/1) shows that the sample is not simply the *tert*-butyl cation. It probably consists of a combination of ionized and un-ionized chloride and inevitably some adventitious hydrocarbon. The Cl 2p core-level spectrum does not help in quantifying the ion pair/neutral molecule ratio. Clearly, though, the low-intensity high binding energy component of the initial C 1s spectrum is attributable to the formation of a localized carbocation center. The major C 1s component must contain a contribution from the three methyl carbon atoms of the cation; fitting such a peak into the more intense C 1s component (dotted curve in Figure 1) shows that the internal shift of this cation would be at least 3.1 eV.

Following consecutive deposition of the Lewis acid and organic halide, at  $-120^{\circ}\text{C}$ , broadening of the C 1s signal over some 30 min suggested that some polarization might be occurring, but a discrete high binding energy peak was not observed. The failure of this type of experiment, attempting ionization specifically in the condensed phase, contrasts sharply with the success of the codeposition (Figure 1) and leads to the conclusion that observation of the cation follows condensation of products of a gas-phase reaction; the immediate observation of cations after a codeposition would then be in agreement with other recently reported results, suggesting that, at low temperature in the condensed phase, bulk ionization of the chloride may take at least several hours to occur.<sup>23</sup>

In the codeposition, gas-phase reactions might be caused by the reagent beams crossing prior to condensing onto the substrate, but this possibility appears to be ruled out by the fact that the same results were obtained using concentric beams. The more likely explanation is that the deposition pressure used ( $\sim 6 \times 10^{-4}$  T) is too great to permit real molecular "beams" and that gas-phase reaction at this pressure is inevitable. However, experiments using lower pressure or dilution of the reagents with an inert gas showed that a high pressure of alkyl halide was necessary for cation formation.

A reaction that would probably accompany gas-phase ionization is the elimination of hydrogen chloride from the organic halide; this would lead to some independence in the carbon and chlorine signal intensities and may explain why the observed carbon/chlorine ratios (3 and 2.5) are less than that expected for a pure *tert*-butyl chloride sample. A complicating feature of this codeposition would therefore be the possibility of a cation-olefin reaction; however, such a product would still be a tertiary cation with a localized positive charge.

In view of the length of time apparently required for ionization at  $-120^{\circ}\text{C}$ , for samples prepared by consecutive deposition, attempts were made to induce ionization by allowing them to warm up, but this approach was unsuccessful. Initially, a surface layer of organic halide tends to "pump off" before ionization occurs, and a lower layer does not appear to migrate to the surface until  $\sim +15^{\circ}\text{C}$  after melting of the Lewis acid has occurred; at this temperature, while some ionization does appear to have occurred, the potential cation peak is superimposed upon a broad high binding energy tail, and this, the comparatively high C/Cl ratio, and the presence of organic fluorine show that side reactions are occurring along with ionization. In addition, it should be noted that while it was of interest to explore such a method for generating the *tert*-butyl cation, it would not be applicable to less stable cations, which would rearrange. (For example, the *sec*-butyl cation rearranges fairly rapidly to the tertiary ion above  $-40^{\circ}\text{C}$ ).<sup>35</sup>

The results obtained from the attempted ionization of norbornyl chloride using antimony pentafluoride (Figure 2) are presented partly for comparison with the results of the protonation of norbornene and partly to show the difficult nature of the studies since this latter point was the source of some of the criticism of the earlier work.<sup>10</sup>

The carbon spectrum recorded around 70 min after the deposition resembles that expected for a classical cation, with a peak  $\sim 8\%$  of the spectral intensity some 3.9 eV to higher binding energy from the main component. The high binding energy peak con-

tinued to grow in intensity and in the final spectrum is  $\sim 25\%$  of the total C 1s intensity; at this stage, the peak is most likely attributable to organic fluorine species,<sup>36</sup> which have been observed in other experiments employing antimony pentafluoride. This puts in doubt whether the second C 1s spectrum in the series is a classical cation or merely an intermediate between norbornyl chloride and the contaminated surface. Assuming that the high binding energy peak is derived from the presence of organic fluorine, the corresponding fluorine intensity can be calculated; the intensity, though not the position, is shown in the fluorine spectrum (dotted line), and it is clear that this could easily be masked by the strong inorganic fluorine peak. It should be emphasized that this particular C 1s spectrum was only seen once, and on other occasions only modest broadening of the C 1s peak of the norbornyl chloride was observed. Bearing in mind that successful ionization of *tert*-butyl chloride was not obtained under these conditions, it would be inappropriate to conclude that this was a positive observation of a classical norbornyl cation.

Until now the majority of spectroscopic studies of carbocations have been performed on samples prepared by the ionization of halides rather than the protonation of alkenes. The protonation of norbornene (bicyclo[2.2.1]hept-2-ene), as a route to the norbornyl cation, is established, but protonation by Magic acid ( $\text{HSO}_3\text{F-SbF}_5$  or  $\text{HF-SbF}_5$ )<sup>37</sup> was not considered feasible because it involves essentially three reagents, increasing the problems in preparing samples for ESCA analysis. However, use of fluorosulfonic acid on its own has been reported to give *exo*-2-norbornyl fluorosulfate.<sup>38</sup> One advantage of using this acid is that the presence of three core levels (F 1s, O 1s, S 2p) enables further information about the state of the system to be derived; hydrolysis of the acid leads to a decrease in F/S ratio and an increase in that of O/S, and while deposition of organic species on top of the acid complicates the situation because of differential attenuation of electrons of different kinetic energies,<sup>39</sup> it is to some extent possible to determine whether degradation of the sample under analysis has occurred.

From the analysis of the norbornene precursor on its own, it is evident that, under the conditions of these experiments, deposition on a gold surface did not occur at  $-120^{\circ}\text{C}$ . Consequently, for deposition to occur in the fluorosulfonic acid-norbornene experiment, there must be some interaction between the precursors. Not only was the C 1s spectrum (Figure 3D) stable for a short period of time ( $\sim 15$  min), but its essential shape was also reproduced in other experiments; this suggests that it is derived from a discrete species. It is also apparent that it is very similar to that previously reported following a very different preparation.<sup>7</sup> For these reasons, it is assigned as the C 1s core-hole spectrum of the norbornyl cation. From the previous work on the *tert*-butyl cation and the ionization of norbornyl chloride, it is evident that the lifetime of carbocation surface can be expected to be quite limited, and the spectrum shown in Figure 3E can therefore be assigned as the degraded cation.

Curve fitting of the norbornyl cation spectrum (Figure 3D) has been based on the SCF STO-4.31G calculations previously reported;<sup>34</sup> this level of theory is known to be accurate enough to calculate internal core-hole shifts and has recently been used to rationalize the experimentally observed cyclopentyl cation C 1s spectrum.<sup>40</sup> The calculation for the norbornyl cation showed that resolution of the observed spectrum in terms of only two components would be incorrect; while the nonclassical ion is expected to be composed of three peaks of relative intensity 2/1/4, the classical ion would ideally be interpreted as four peaks of ratio 1/2/1/3 (Table I).

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Table I

	a	b	c
Classical			
C <sub>2</sub>	4.4	1	2.6
C <sub>3</sub>	1.4	2	1.5
C <sub>1</sub>	1.3		
C <sub>6</sub>	0.8	1	0.3
C <sub>4</sub>	0.3	3	0.0
C <sub>7</sub>	0.3		
C <sub>5</sub>	(0.0)		
Nonclassical			
C <sub>1</sub> , C <sub>2</sub>	2.0	2	2.0
C <sub>6</sub>	1.2	1	0.9
C <sub>3</sub> , C <sub>7</sub>	0.3	4	0.0
C <sub>4</sub>	-0.1		
C <sub>5</sub>	(0.0)		

<sup>a</sup>SCF STO-4.31G shifts<sup>34</sup> (eV). <sup>b</sup>Expected peak group intensities. <sup>c</sup>Shift found in simulation of experimentally observed spectrum [Figure 3D (eV)].

Additionally, in interpreting the experimental spectrum, the possible presence of adventitious hydrocarbon has been modeled by allowing it to contribute to the most intense, low binding energy component in each case.

It has been found that the experimental spectrum can be well represented either by three peaks, fwhm  $\sim 1.7$  eV, in the intensity ratio 4/2/13 (a nonclassical model) or by four peaks fwhm  $\sim 1.5$  eV in the intensity ratio 2/4/2/11 (a classical model). It is interesting to note that both models suggest that up to  $\sim 25\%$  of the observed spectrum might be attributable to surface hydrocarbon. On the basis solely of the predicted component intensity ratios, therefore, the observed spectrum cannot be considered to be diagnostic of either a classical or nonclassical structure. However, as originally pointed out,<sup>5</sup> the single most important parameter of carbocation spectra is perhaps the internal shift; these shifts for the two models are summarized in Table I together with the experimental values. In the classical species, the carbon bearing the positive charge is expected to be some 4.4 eV to higher binding energy of the most intense spectral component, whereas in the simulated experimental spectrum this important internal shift is only  $\sim 2.6$ , the 1.8 eV difference between experimental and theoretical values being far beyond the expected error of the calculations. In contrast to this inconsistency assuming a classical model, the simulation of line shape on the basis of a nonclassical model suggests an internal shift of 2.0 eV for C<sub>1</sub> and C<sub>2</sub> from the major component, in excellent agreement with the calculated value. Agreement between the calculated and observed shift for C<sub>6</sub> in the nonclassical ion (1.25 and 0.9 eV, respectively) is not quite as good, but it should be noted that a comparison of the MINDO/3<sup>41</sup> and ab initio results show that the charge at C<sub>6</sub> is somewhat geometry dependent.<sup>42</sup> Thus, on the basis of line shape and internal shift analysis, the C 1s spectrum observed when norbornene is reacted with fluorosulfonic acid is consistent with nonclassical models and not with classical ones.

The first C 1s spectrum obtained after the introduction of butene (Figure 4B) is assigned as that of the *sec*-butyl cation; at this point, the butene must have reacted because it was previously shown that its deposition on a gold surface is problematical even at a lower temperature. The observed core-hole spectrum is not that appropriate to the alkene precursor nor that of polymerized butene, which would lead to only one peak. A quenched cation (butan-2-ol) would lead to two peaks, intensity ratio 1/3, and an internal shift of  $\sim 1.6$  eV;<sup>43</sup> while the *sec*-butyl cation is known to easily undergo rearrangement to the tertiary cation, the internal shift of the observed spectrum is inconsistent with this.<sup>5</sup> The reproducibility of the spectrum suggests that it corresponds to a

discrete species rather than to a mixture produced from quenching, fluorination, isomerization, and polymerization, since these side reactions would be expected to vary in different experiments. The main motivation for varying the inlet pressure of butene was in order to try to ascertain whether excess alkene might be contributing to the lower binding energy component, but since the relative intensity of this was independent of the amount of butene introduced, it appears that this is not a problem. The later, more complex, C 1s spectrum (Figure 4C) is considered to be a degraded form consistent with the growing hydrolysis of the acid bed, and this can be inferred from observation of the F 1s, O 1s, and S 2p core levels.

At first sight, the *sec*-butyl cation spectrum (Figure 4B) does appear to be simply two peaks, i.e. two carbon environments, but is not possible to curve fit the line shape with only two Gaussians of the same fwhm. Fitting as two peaks (internal shift  $\sim 2.1$  eV) requires that the lower intensity peak to higher binding energy has a half-width some 40% greater than the other; in addition, the two peaks would have an intensity ratio of 1/2, which has no chemical meaning in relation to a four carbon atom system. Thus, a two-peak fit of the spectral line shape is purely mathematical, and the anomalies in fwhm and intensity ratio show that the resolution is more complex. Using four Gaussian peaks of equal half-widths and intensities suggests that the maximum separation of the two of lowest binding energy is  $-0.2$  eV so that the spectrum can be well reproduced with only three peaks of ratio 1/1/2. The internal shifts are  $\sim 2.5$  and  $\sim 0.9$  eV from the most intense component. By comparison with the core-hole calculations, the span of energies is clearly inconsistent with an essentially localized positive charge ( $\sim 6.1$  eV, C<sub>3</sub>;  $\sim 4.7$  eV, C<sub>1</sub>) while the presence of three carbon environments rules out the possibility of the H-bridged cation structure. The shape of the observed spectrum suggests a partially methyl-bridged structure on the basis that the spectrum of this is predicted to have components of intensity ratio 1/1/2 in contrast to the fully bridged ion, which should be 2/1/1 (high to low binding energy). The internal shift of C<sub>3</sub>, from C<sub>1</sub>, is calculated to be 0.3 and 1.9 eV in the partially and fully methyl-bridged structures, respectively, compared with the experimental value of 0.9 eV. The span of binding energies, experimentally determined as 2.5 eV, is intermediate between those for the partially (3.1 eV) and fully (2.1 eV) bridged cations. From this it appears that the structure of the *sec*-butyl cation is intermediate between the partially and fully bridged geometries considered theoretically for this cation, and it is perhaps best described as substantially methyl bridged.

Finally, it is in order to give a brief comparison of the two methods that have permitted ESCA analysis of carbocations. The advantage of Olah's "frozen-solution" approach is that it allows the use of multicomponent superacid systems (e.g. HSO<sub>3</sub>F-SbF<sub>5</sub>-SO<sub>2</sub>) or systems that may be slow in reaching equilibrium (e.g. RCl-SbF<sub>5</sub>). The method is therefore more versatile. The disadvantage is the experimental difficulty of trying to introduce cooled probes into the spectrometer. The in situ method also has the positive advantage that it permits analysis of the acid surface prior to introduction of the organic precursor thus ensuring the authenticity of the carbocation C 1s signal.

## Conclusions

The internal shift of a carbocation with a localized positive charge is  $\geq 3.1$  eV, as expected from earlier results. The codeposition of antimony pentafluoride and *tert*-butyl chloride leads to the observation of carbocations following a gas-phase reaction, and the condensed-phase ionization proceeds too slowly to be useful for in situ preparation. In contrast, the protonation of alkenes by fluorosulfonic acid appears to proceed rapidly and permitted the preparation of the 2-norbornyl and *sec*-butyl cations under stable ion conditions. On the basis of component intensity and internal shifts, the observed C 1s core-hole spectrum of the 2-norbornyl cation is consistent with a nonclassical structure; this result confirms the validity of the first ESCA experiments,<sup>5-8</sup> which yielded proof of the nonclassical nature of the norbornyl cation. Similar analysis of the C 1s core-hole spectrum of the *sec*-butyl

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cation shows that it is closest to that theoretically predicted for a partially methyl-bridged structure.

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**Registry No.** Antimony pentafluoride, 7783-70-2; *tert*-butyl chloride, 507-20-0; *exo*-2-norbornyl chloride, 765-91-3; 2-norbornene, 498-66-8; fluorosulfonic acid, 7789-21-1; *cis*-but-2-ene, 590-18-1; *tert*-butyl cation, 14804-25-2; 2-norbornyl cation, 24321-81-1; *sec*-butyl cation, 16548-59-7.

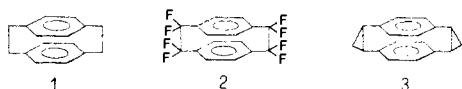
## $\sigma/\pi$ Interactions in [2.2]Paracyclophanes. PE Investigations on Octamethyltetrasila[2.2]paracyclophane and Octamethyltetrasila[2.2](2,5)thiophenophane and -furanophane

Rolf Gleiter,<sup>\*,†</sup> Wolfgang Schäfer,<sup>†</sup> Gerhard Krennrich,<sup>†</sup> and Hideki Sakurai<sup>\*,‡</sup>

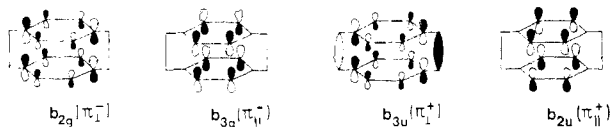
Contribution from the Institut für Organische Chemie, Universität Heidelberg, D-6900 Heidelberg, West Germany, and Department of Chemistry, Tohoku University, Sendai 980, Japan. Received November 13, 1987

**Abstract:** The photoelectron spectra of 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetrasila[2.2]paracyclophane (**6a**) and the related octamethyltetrasila[2.2](2,5)thiophenophane (**7a**) and -furanophane (**8a**) have been recorded. The sequence of the first bands of these spectra is assigned by comparison of the ionization energies with calculated orbital energies. A comparison between the band sequence of **6a** and that of [2.2]paracyclophane (**1**) shows a smaller through-space and a larger through-bond interaction for **6a**. The through-bond interaction between the  $b_{3u}(\sigma)$  orbital and the corresponding  $\pi$  orbital yields a different orbital sequence in **6a** as compared to **1**. A similar strong through-bond interaction as in **6a** has been encountered in **7a** and **8a** as shown by comparing the PE spectra of the latter compounds with [2.2](2,5)thiophenophane (**10**) and [2.2](2,5)furanophane (**11**).

The He I photoelectron (PE) spectrum of [2.2]paracyclophane (**1**) shows a broad first band between 8.0 and 8.4 eV, well separated from two smaller bands at 9.65 and 10.3 eV.<sup>1</sup> It is generally



accepted that the first feature is due to the three different ionic states  ${}^2B_{2g}$ ,  ${}^2B_{3g}$ , and  ${}^2B_{3u}$  while the second band is assigned to  ${}^2B_{2u}$ .<sup>1,2</sup> A schematic drawing of the corresponding wave functions is given. A consideration of the wave functions corresponding



to the four highest occupied MO's of **1** shows that the MO's that pertain to the irreducible representations  $b_{3g}$ ,  $b_{2g}$ , and  $b_{2u}$  are pure  $\pi$  MO's, while  $b_{3u}$  has a considerable admixture of the C-C  $\sigma$  bonds connecting the two rings.<sup>2,3</sup> This difference in  $\sigma/\pi$  interaction can be used to investigate the sequence of the corresponding bands empirically. The  $\sigma/\pi$  mixing of the  $b_{3u}$  orbital can be increased or decreased by lowering or raising the energy of the  $b_{3u}(\sigma)$  orbital, which interacts with  $b_{3u}(\pi)$ . An increase of  $b_{3u}(\sigma)$  will increase  $\sigma/\pi$  mixing and thus will lower the orbital energy of  $b_{3u}$  and vice versa.

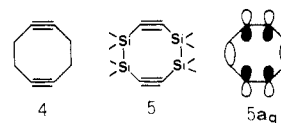
Heilbronner and Maier<sup>4</sup> have studied a case where the  $\sigma/\pi$  interaction is lowered by investigation of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (**2**). Due to the inductive effect of the fluorine atoms, the ionization from the  $b_{3u}$  orbital of **2** occurs at considerably higher energy than from  $b_{2g}$  and  $b_{3g}$ . The opposite effect can be detected in the PE spectrum of [1,2:9,10]di-

**Table I.** Comparison between the Measured Ionization Energies,  $I_{v,j}$ , of **6a** and the Orbital Energies,  $\epsilon_j$ , Calculated for **6b** Using the FMO Approach and the MNDO and the ab Initio Methods

band	$I_{v,j}$	assignment	$-\epsilon_j(\text{FMO})$	$-\epsilon_j(\text{MNDO})$	$-\epsilon_j(\text{STO-3G})$
1	7.8	$6b_{3u}$	7.84	8.46	6.27
2	8.3	$\begin{cases} 5b_{2g} \\ 5b_{3g} \end{cases}$	8.20	8.76	6.33
3	9.2	$5b_{2u}$	9.40	9.98	7.10
4	9.8	$7a_g$	10.60	9.33	7.89

methano[2.2]paracyclophane (**3**).<sup>5</sup> In this compound the basis orbital energy of the  $\sigma$  bond of the three-membered rings in **3** is higher than the  $\sigma$  bonds in **1**, which leads to an increase of the  $\sigma/\pi$  interaction and thus lowers the energy associated to the ionization from the  $b_{3u}(\pi)$  orbital. Due to the strong overlap of the first three PE transitions, the expected shift is, however, difficult to recognize.

Recently,<sup>6</sup> we have shown that the replacement of a C-C  $\sigma$  bond in **4** by a Si-Si  $\sigma$  bond, **5**, has dramatic effects on the sequence of the highest occupied MO's. A comparison of the PE spectra



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