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SHORT COMMUNICATION

VIBRATIONAL SPECTRA OF $C_4H_7^+$ ISOMERS IN LOW-TEMPERATURE ANTIMONY PENTAFLUORIDE MATRICES

H. VANČIK,* V. GABELICA AND D. E. SUNKO*

Department of Chemistry, Faculty of Science, University of Zagreb, Strossmayerov trg 14, 41000 Zagreb, Croatia

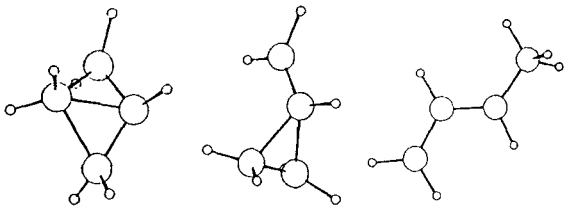
AND

P. BUZEK AND P. v. R. SCHLEYER*

Institut fur Organische Chemie der Friedrich-Alexander Universitat Erlangen–Nuernberg, Henkestr. 42, D-8520 Erlangen, Germany

The IR spectra of isomeric bicyclobutonium (1), delocalized cyclopropylcarbinyl (2) and 1-methylallyl (3) cations were recorded at 180 K in SbF_5 matrices. Cations 1 and 2 generated from cyclopropylcarbinyl and cyclobutyl chloride, respectively, rearrange to 3 at temperatures above 230 K. The structures 1, 2 and 3 were confirmed by comparison of the recorded frequencies with the MP2/6–31G*-calculated values. These results are in accord with prediction that ions 1 and 2 are rapidly equilibrating non-classical structures.

In the word of J. D. Roberts,[1a] the structure of $C_4H_7^+$, the very first 'nonclassical' carbocation, 'has truly been and still is a chemical chimera.' He does not agree that all the earlier evidence[1] and even the advent of high level *ab initio* computations,[2] the ability to calculate ^{13}C chemical shifts (IGLO) with high accuracy,[2b] and the CP MAS experiments of Myhre and Yannoni down to 5K[3] establish that two isomers of nearly equal energy – the symmetrical bicyclobutonium ion (**1**) and the cyclopropylcarbinyl cation (**2**) – are in rapid equilibrium. Roberts calls for 'new ways of investigating $C_4H_7^+$', such as infrared spectroscopy. We now answer this request. These results, which indicate the presence of two isomers of nearly equal energy, the bicyclobutonium ion (**1**) and a delocalized cyclopropylcarbinyl cation (**2**), as the most probable structures of the ion generated from cyclopropylcarbinyl or cyclobutyl precursors, supported the evidence obtained earlier from deuterium isotope effects studies by Saunders and Siehl.[2d] The computed (IGLO) chemical shifts fit best with a mixture of **1** and **2**, with the former predominating.[2b] The cross-polarization magic angle spinning NMR experiments of Myhre *et al.*[3] confirmed the theoretical calculations and demonstrated that the two



(1) (2) (3)

isometric ions are in rapid equilibrium even at temperatures as low as 5 K. Theory[2] also predicts that the thermodynamically most stable isomer is the 1-methylallyl cation **3**.

Using the recently developed[4] matrix isolation technique for generating carbocations, we have now obtained the Fourier transform spectra of ions produced in the reaction of cyclopropylcarbinyl chloride and cyclobutyl chloride with SbF_5 at 77–200 K in the matrix. The procedure started with codeposition of each chloride and SbF_5 on the cooled CsI window at 77 K. At this temperature the IR spectra reveal only the starting materials [Figures 1(a) and 2(a)]. The different stages of the ionization of cyclopropylcarbinyl chloride are shown in Figure 1. The new signals which appear

* Author for correspondence.

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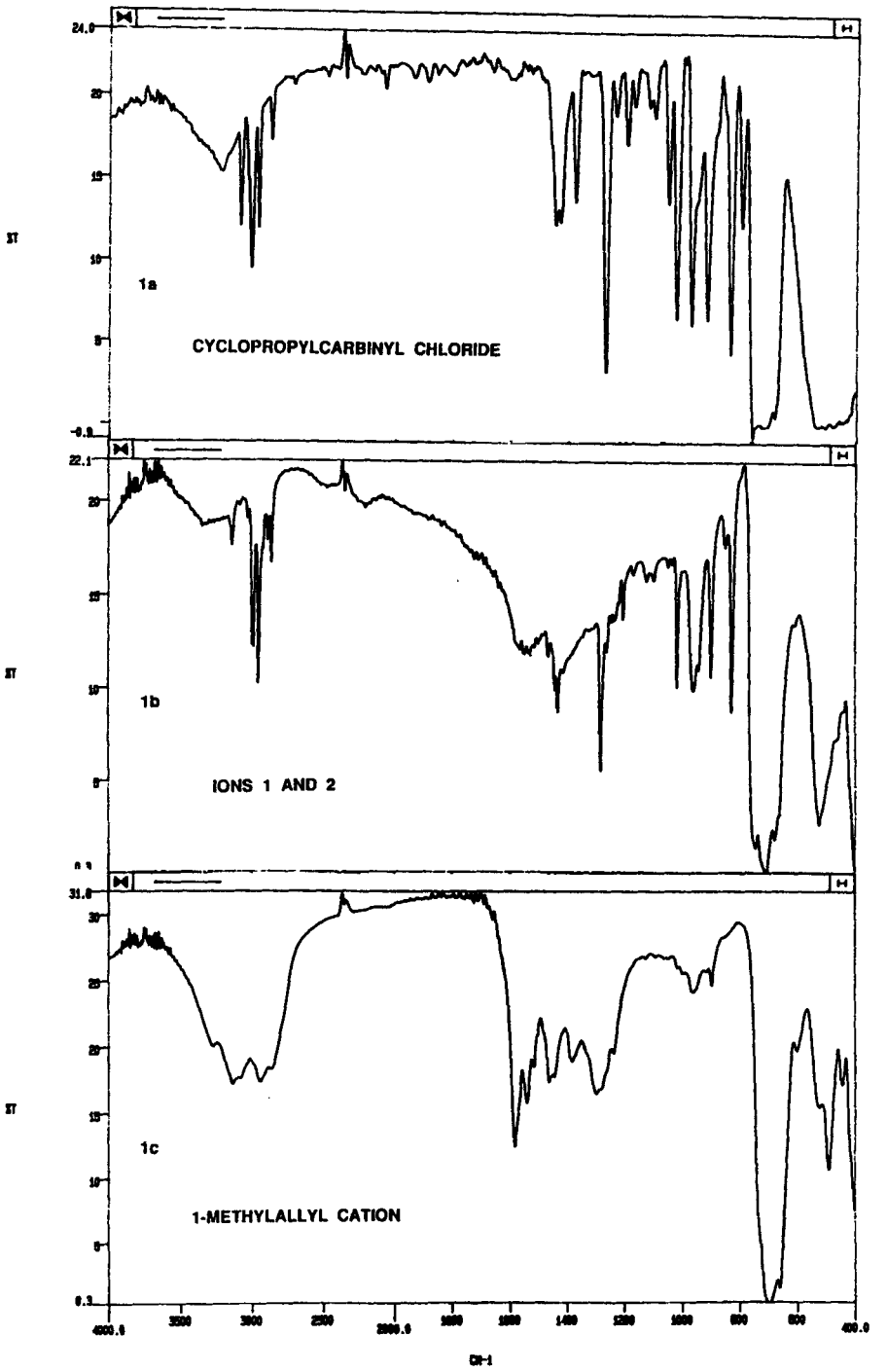

Figure 1. IR spectra of (a) cyclopropylcarbinyl chloride in SbF_5 matrix at 77 K; (b) the resulting mixture of **1** and **2** at 200 K; (c) **3** at 230 K

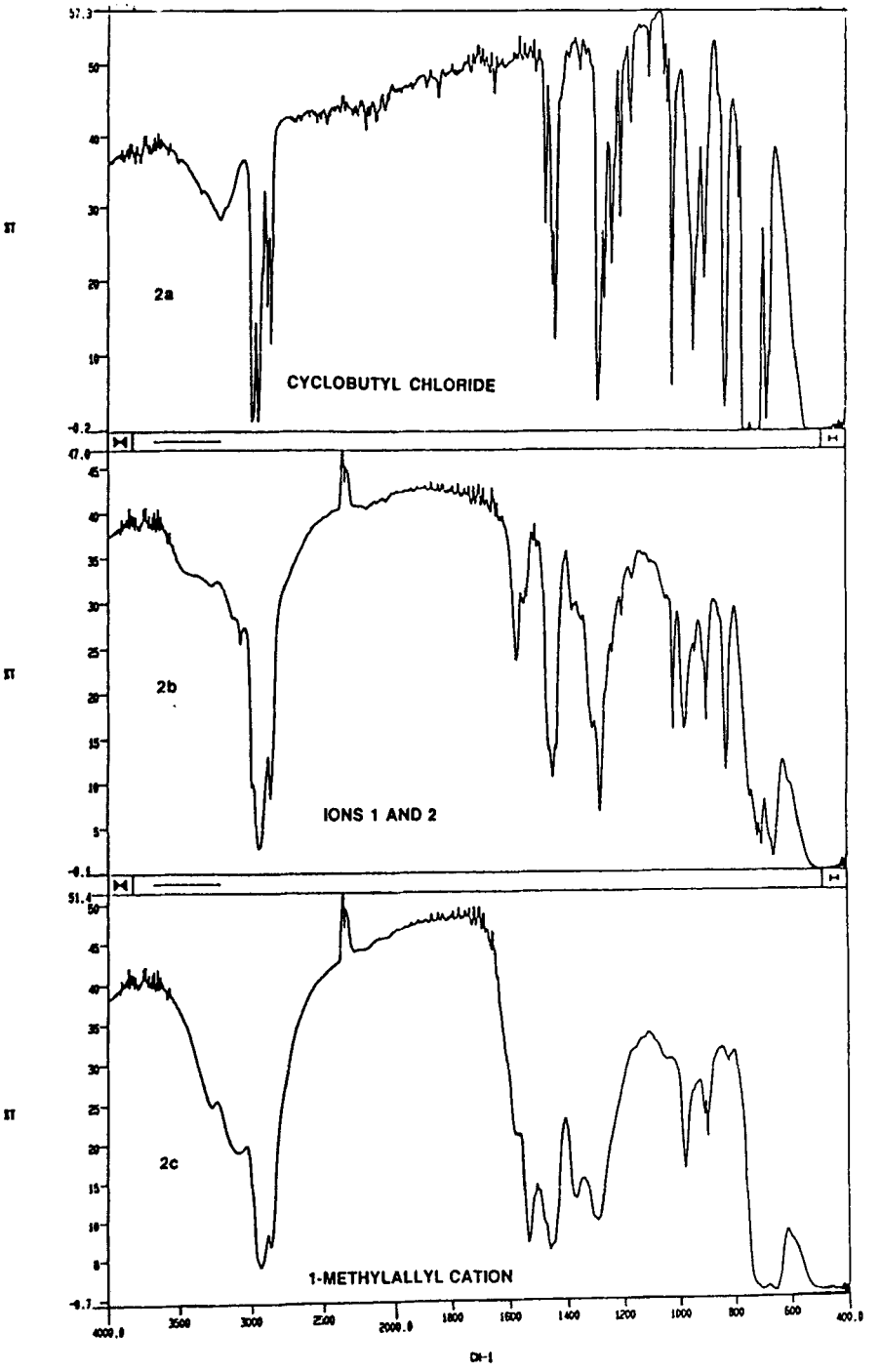

Figure 2. IR spectra of (a) cyclobutyl chloride in SbF_5 matrix at 77 K; (b) the resulting mixture of **1** and **2** at 200 K; (c) **3** at 230 K

below 180–200 K [Figure 1(b)] disappear at 230 K and a new spectrum develops [Figure 1(c)]. The same experiment was repeated with cyclobutyl chloride; the spectra are presented in Figure 2.

The main difference between the spectra in Figures 1(b) and 2(b) is in their relative intensities, whereas the spectra in Figures 1(c) and 2(c) are identical in every respect. The bands which appear at lower temperatures Figures 1(b) and 2(b)] could be best fitted with the *ab initio* MP2/6–31G*-computed frequencies for a combination of frequencies for the bicyclobutonium ion (**1**) and the cyclopropylcarbinyl cation (**2**) by assuming that both isomers are present at temperatures below 200 K (Table 1). The experimental spectrum is compared with the spectrum calculated for the mixture of ions **1** and **2** in Figure 3. The appearance of both cations **1** and **2** at temperatures below 200 K confirms the IGLO[2b] NMR results[3] and also the small theoretical energy difference between[2] these ions.

The spectrum at higher temperatures is due to the 1-methylallyl cation[5] (**3**) [Figures 1(c) and 2(c)]. The 1-methylallyl cation was also produced independently from crotyl chloride (**4**) and from homoallyl bromide (**5**) (Figure 4). Attempts to prepare the homoallyl cation **6** from **5** resulted in the formation of **3**, in agreement with the theoretical prediction that this cation is not a minimum on the MP2/6–31G* potential energy surface[2] (Figure 4).

Cation **3** is the simplest allyl cation observable in a superacid medium. The experimental IR frequencies

Table 1. Calculated (MP2/6–31G*) and experimental frequencies of bicyclobutonium (**1**) and cyclopropylcarbinyl (**2**) cations (scaling factor 0·94)

1 + **2** (exp.)(cm^{-1})	**1** (calc.)(cm^{-1})	**2** (calc.)(cm^{-1})
3138	3169	3170
3013	3080	3156
2990	3057	3150
2947	3053	3128
2859	3045	3056
		3053
1572	1489	1570
1467	1483	1502
1450	1395	1432
1432	1392	1384
1280	1214	1264
1238	1124	1227
1203	1088	1094
1123		
1101		
1022	1034	1078
971	931	1037
945	898	975
905	859	
839	744	

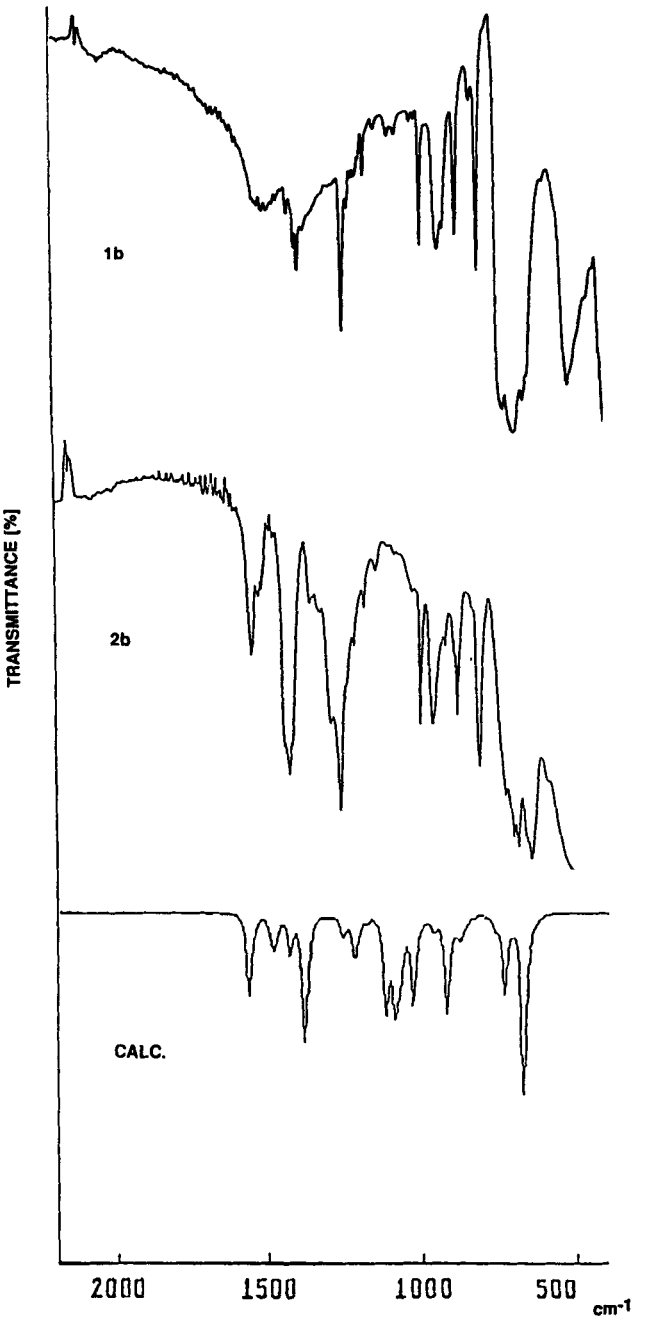

Figure 3. Experimental and calculated[2a] (scaling factor 0·94) IR spectra of a 1:1 mixture of **1** and **2**

Figure 4. IR spectra of 1-methylallyl cation generated from (a) homoallyl bromide and (b) from crotyl chloride (the signals of unknown byproduct are labelled with arrows)

Table 2. Calculated (MP2/6–31G*) and experimental frequencies of methylallyl cation **3** (scaling factor 0·94)

Experimental (cm^{-1})	Calculated (cm^{-1})	Experimental (cm^{-1})	Calculated (cm^{-1})
3085	2966	1296	1310
2937	2905		1277
1581	1604		1244
1536	1497		1161
1462	1419		1075
1371	1399	982	979
	1324	911	966
			852

compare well with the calculated values (Table 2). The characteristic group frequency for the allyl cation is asymmetric $[C{=}{=}C{=}{=}C]^+$ stretching vibration at 1581 cm^{-1} (the MP2/6–31G*-calculated frequency is 1604 cm^{-1}). The 3085 cm^{-1} frequency is assigned to the C–H stretching vibration.

In keeping with the suggestion that 'infrared or Raman spectra at 5 K could solve this problem,'[1a] this work presents direct spectroscopic evidence that $C_4H_7^+$ is best represented by rapidly equilibrating non-classical structures **1** and **2** of nearly identical energy. At higher temperatures the mixture of **1** and **2** rearranges to the methylallyl cation **3** which is persistent under the superacid conditions in the condensed phase. It is gratifying to see how some of the very early hypotheses[1i,6] regarding the structure of these small but elusive species, which were first based on indirect, mostly solvolytic evidence, are now confirmed by, *inter alia*, IR spectroscopy.

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