SUPPORTING INFORMATION

An IR-spectroscopic and X-ray-structural study of vinyl-type carbocations in their carborane salts

Evgenii S. Stoyanov, Irina Yu. Bagryanskaya and Irina V. Stoyanova*

N.N. Vorozhtsov Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, 9 Ak. Lavrentieva Avenue, Novosibirsk 630090, Russian Federation.

* Corresponding author. E-mail address: evgenii@nioch.nsc.ru

IR spectral data

Table S1.

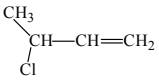
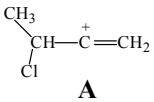
The most indicative frequencies of the $C_4H_8Cl^+$ cation in ATR IR spectra of its salts with anion $\{F_{11}^-\}$ or $\{Cl_{11}^-\}$

Anion	C-H stretch vibrations	H-C-H and C-C-H bent vibrations			νCC	ν_{as}C-Cl$^+$-C
$\{F_{11}^-\}$	3079 2967 2929	1443	1435	*	*	584
$\{Cl_{11}^-\}$	3050 2985 2971 2945	1429	1436	1252	883	582

*Overlapped with strong absorption of the $\{F_{11}^-\}$ anion.

Table S2.

The most characteristic frequencies of isomer **A** in its salts with the $\{Cl_{11}^-\}$ anion in comparison with those of neutral 3-chloro-1-butene[a] (we do not show vibrations whose frequencies in IR spectra of the cations overlap with the intense absorption pattern of anion $\{Cl_{11}^-\}$)

 solid	 **A**	Assignment [a] Approximate description
3084 s	[b]	$=CH_2$ asym stretch
3011 w	[b]	=CH stretch
2986 s	[b]	$=CH_2$ sym stretch
2974 vs	2960	CH_3 asym stretch
2927s	2928	CH_3 sym stretch
2880	2872	Combination
1637 m	1680 s	C=C stretch
1446 s	1446	CH_3 asym deformation
1372 vs	1373	CH_3 sym deformation
1307 w	1301	CH bend
		$=CH_2$ rock
1175s	[c]	CC stretch
862s		
1096 m	1093 w	CH_3 rock
708 s	770 s	C-Cl stretch

[a] Lee, M. J., Fusheng, F., Hur, S. W., Liu, J., Gounev, T. K., Durig, J. R. Raman and infrared spectra, conformational stability, normal coordinate analysis and ab initio calculations of 3-chloro-1-butene. J. Raman Spectrosc. 2000, 31, 157-169; [b] it is assumed that the protons of groups $=CH_2$ and =CH participate in fast proton exchange and do not yield narrow absorption bands in the IR spectra; [c] the frequencies of CC stretches of the cation differ significantly from those of a neutral molecule and were not identified with certainty

Table S3. The most characteristic frequencies of an IP in isomer **IV** of cation $C_4H_7^+$ in its salt with the $\{Cl_{11}^-\}$ anion in comparison with those of neutral compound 1-butene (we do not show cations' vibrations whose frequencies overlap with the intense absorption pattern of anion $\{Cl_{11}^-\}$)

CH_3 / CH_2—CH═CH_2 cis / trans; gas [a]	CH_3 / CH_2—C^+═CH_2 **IP** of isomer **IV**	Assignment [a] Approximate description
3090	3112	=CH_2 asym stretch
3019	*b*	=CH stretch
3008	3056	=CH_2 sym stretch
2982 2978	2850	CH_3 asym stretch
2952 2948	2811	CH_3 sym stretch
2936	*b*	CH_2 asym stretch
2888	*b*	CH_2 sym stretch
-	2743	Combination
1643 1647	1588	C=C stretch
1460 1463	1460	CH_3 asym deformation
1450 1444	1441	CH_2 deformation
1426 1421	1412	=CH_2 deformation
1380	1380	CH_3 sym deformation
1342 1318	*b*	CH_2 wag
1071 1079	1076	=CH_2 rock
988 1020	*c*	CC stretch
836 854		

[a] R. Durig, D. A. C. Compton. Spectroscopic and Thermodynamic Study of the Conformational Properties and Torsional Potential Functions of 1-Butene. *J. Phys. Chem*. 1980, 84, 773-781; [b] not determined; [c] the frequencies of CC stretches of the cation differ significantly from those of a neutral molecule and were not identified with certainty.

Crystal phase data

Table S4

Crystallographic data and details of the XRD experiment

Compound	Salt of isomers **A/B**	Salt of isomer **III**	Salt of isomers **I/II**
Empirical formula	$C_4H_6Cl + CHB_{11}Cl_{11}$	$C_4H_7+C_4H_8+CHB_{11}F_{11}$	$C_4H_7 + CH\ B_{11}Cl_{11}$
Formula weight	611.42	452.13	576.97
Temperature K	200(2)	200(2)	200(2)
Wavelength Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pnma	$P2_1/c$	$P2_1$
Unit cell dimensions *a* Å	14.7756(8)	8.252(3)	9.241(3)
b Å	11.9476(7)	11.928(4)	13.060(4)
c Å	12.6233(8)	9.977(4)	10.830(4)
α °	90	90	90
β °	90	105.841(11)	102.475(12)
γ °	90	90	90
Volume $Å^3$	2228.4(2)	944.7(6)	1276.2(7)
Z	2	2	2
Density (calcd.) $Mg.m^{-3}$	1.822	1.589	1.501
Abs. coefficient mm^{-1}	1.485	0.159	1.190
F(000)	1184	448	560
Crystal size mm^3	0.1 x 0.15 x 0.2	0.10 x 0.20 x 0.30	0.08 x 0.15 x 0.20
Θ range for data collection °	2.1 – 26.0	2.6 - 25.1	2.3 – 26.1
Index ranges	$-18 \le h \le 18$, $-14 \le k \le 14$, $-15 \le l \le 15$	$-9 \le h \le 9$, $-14 \le k \le 14$, $-11 \le l \le 11$	$-10 \le h \le 11$, $-16 \le k \le 16$, $-13 \le l \le 13$
Reflections collected	37223	11028	12368
Independent reflections	2300 R(int) = 0.049	1680 R(int)= 0.068	5024 R(int)= 0.056
Completeness to θ %	99.8	99.1	99.4
Data / restraints / parameters	2300 / 111 / 199	1680 / 56 / 172	5024/ 182 / 275
Goodness-of-fit for F^2	1.16	1.04	1.07

Final R indices $I > 2\sigma(I)$	R_1=0.0626, wR_2 = 0.1635	R_1 = 0.1537, wR_2 = 0.3426	R_1 = 0.0736, wR_2 = 0.1995
Final R indices (all data)	R_1=0.0739, wR_2 = 0.1697	R_1=0.2256, wR_2 = 0.3860	R_1=0.0975, wR_2 = 0.2178
Largest diff. peak / hole e.Å^{-3}	1.23/ -0.81	0.70 / -0.56	2.5 / -0.63

Table S5. Selected bond lengths and bond angles for isomers **A** and **B** of cation $C_4H_7Cl^+$ in the salt with the $CHB_{11}Cl_{11}^-$ counterion

Isomer **A**		Isomer **B**	
Bond	Length (Å)	Bond	Length (Å)
C1K1–C3K1	1.33(2)	C1K2–C3K2	1.50(2)
C3K1–C4K1	1.50(3)	C3K2–C4K2	1.33(3)
C4K1–Cl1K	1.96(3)	C4K2–Cl2K	1.75(3)
C4K1–C2K1	1.52(3)	C4K2–C2K2	1.51(3)
Bond angles	(°)	Bond angles	(°)
C1K1–C3K1–C4K1	140(2)	C1K2–C3K2–C4K2	125(2)
C3K1–C4K1–C2K1	143(3)	C3K2–C4K2–C2K2	148(2)

Table S6. Selected bond lengths and bond angles for isomers **I**, **IIa** and **IIb** of cation $C_4H_7^+$ in the salt with the $CHB_{11}Cl_{11}^-$ counterion

Isomer **IIa**		Isomer **IIb**		Isomer **I**	
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
C1–C2	1.47(5)	C3'–C4	1.30(3)	C2"–C3"	1.39(3)
C2–C3	1.39(3)	C3'–C8'	1.55(2)	C2"–C6	1.51(4)
C3–C4	1.55(2)	C4–C7	1.47(4)	C3"–C8"	1.55(2)
Bond angles	(°)	Bond angles	(°)	Bond angles	(°)
C1–C2–C3	129(2)	C4–C3'–C8'	126(2)	C3"–C2"–C6	107(2)
C2–C3–C4	120(2)	C3'–C4–C7	130(2)	C2"–C3"–C8"	120(2)

Table S7. Selected bond lengths and bond angles for isomer **III** of cation $C_4H_7^+$ and a 2-butene molecule in the salt with the $CHB_{11}F_{11}^-$ counterion

Isomer **III**		2-butene	
Bond	Length (Å)	Bond	Length (Å)
C1–C2	1.51(3)	C1'–C2'	1.50(3)
C2–C3	1.34(2)	C2'–C3'	1.35(4)
C3–C4	1.51(3)	C3'–C4'	1.51(3)
Bond angles	(°)	Bond angles	(°)
C1–C2–C3	107(2)	C1'–C2'–C3'	112(2)
C2–C3–C4	126(2)	C2'–C3'–C4'	122(1)