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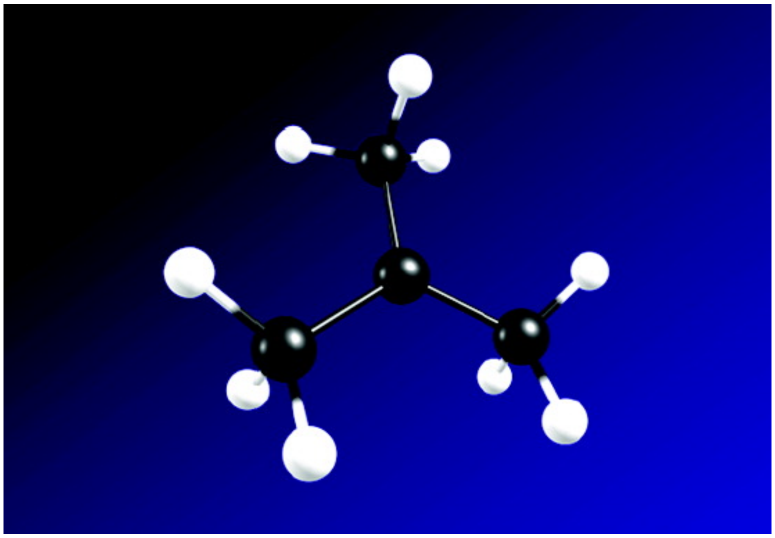

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Infrared Spectroscopy of the *tert*-Butyl Cation in the Gas Phase

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Although Steglitz first proposed tertiary alkyl cations as possible reactive intermediates in organic reactions in 1899,[1] the direct spectroscopic observation of the *t*ert-butyl cation (NMR and IR) in superacid media waited until the achievement of Olah et al. in 1963 (initially via the ready loss of CO from t-$C_4H_9-CO^+$).[2] Carbocations[3] also have been studied extensively in the gas phase by mass spectrometry.[4] The stability of alkyl cations depends on their structure, their degree of substitution, and their charge delocalization due to polarization and hyperconjugation. The *tert*-butyl cation is the archetypical example of a tertiary carbocation with high stability. Its detailed structure is not known experimentally. An X-ray structure has been reported, but the hydrogen positions could not be refined and may be disordered.[5] Possible geometries have been examined thoroughly at various theoretical levels.[6−8] Gas-phase photoelectron spectra provided the ionization energy, but no structural data.[9] We now present the first gas phase infrared spectrum of the *tert*-butyl cation.

Ions were produced by a high voltage discharge in a pulsed supersonic expansion of *tert*-butyl chloride (180 mbar vapor pressure @ 0 °C) and 10% argon seeded in a 70:30 Ne/He mixture. After collimation by a skimmer, the ion-containing molecular beam is sampled with a reflectron time-of-flight mass spectrometer. The use of this instrument for mass-selected ion photodissociation spectroscopy has been described.[10] Infrared spectra were measured using the rare gas tagging method, which is a convenient alternative when absorption spectroscopy is not possible.[10−14] After generation, the weakly bound $C_4H_9^+Ar$ ion complex was excited with a pulsed IR optical parametric oscillator/amplifier (OPO/OPA) laser system (LaserVision) pumped by an injection-seeded Nd:YAG laser (Spectra Physics PRO-230). The $C_4H_9^+$ fragment ion signal versus the infrared wavelength was recorded. The 2000−4000 cm^{-1} frequency range employed a KTP oscillator and KTA amplifier crystals, while the 800−2000 cm^{-1} range employed difference frequency generation in a $AgGaSe_2$ crystal.[15] Ab initio computations at the MP2(fc)/6-311+G(2d,2p) level on various $C_4H_9^+$ geometries with and without argon elucidated the spectra using the GAMESS program package.[16] Computed vibrational frequencies were scaled (0.95)[17] for comparison with the experimental data.

Infrared photodissociation spectra measured for $C_4H_9^+$ species by means of the argon tagging method are shown in Figure 1, along with simulated spectra based on the vibrational frequencies and intensities computed for various isomeric structures. The present calculations with larger basis sets confirm the essential aspects of the previous theoretical work.[6−8] Details of these calculations are provided in the Supporting Information. The stability of the *tert*-butyl cation, well-known to be the $C_4H_9^+$ global energy minimum, is responsible for our unexpected first observation of the t-$C_4H_9^+$ IR spectrum in an ethylene discharge experiment. However, several other $C_4H_9^+$ isomers (e.g., the 2-butyl cation and protonated cyclobutane) may be formed depending on the method of preparation[4−6] and the barriers hindering rearrangement to the *tert*-butyl cation. Figure 1 includes spectra computed for several $C_4H_9^+Ar$ structures. Ar was included since the spectra are measured on tagged species. However, computations with and without argon show that it has a negligible influence on these spectra, consistent with its weak binding (calculated $D_e = 730$ cm^{-1} or 2.1 kcal/mol).

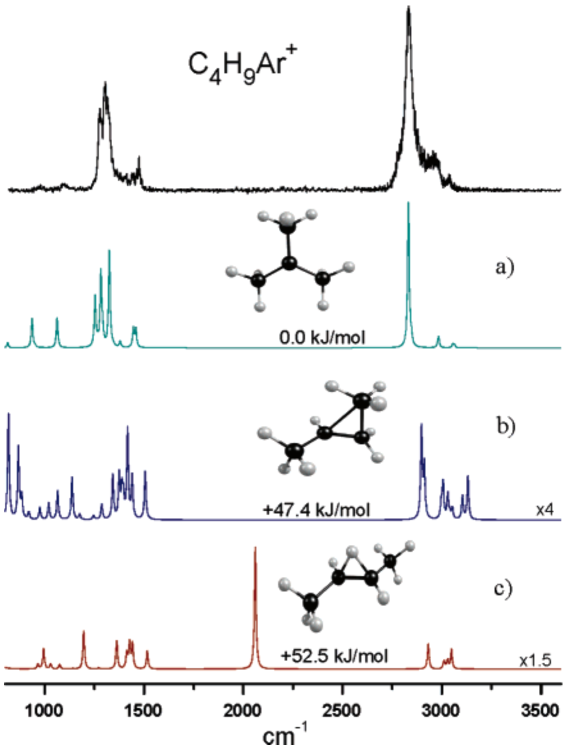

Figure 1. The infrared spectrum measured for Ar-tagged $C_4H_9^+$ compared to the predictions of theory for different Ar-tagged isomers: (a) the spectrum for the C_1 (near-C_s) configuration of the *tert*-butyl cation; (b) the spectrum for the methyl bridged 2-butyl cation, and (c) the spectrum for the proton-bridged 2-butyl cation.

Our experimental $C_4H_9^+Ar$ infrared spectrum (Figure 1, top) features a strong absorption in the C−H stretching region and a multiplet of three bands near 1300 cm^{-1}. Weaker satellites are evident. Table 1 compares our results with theoretical computations and the previous experimental work.[2b] Our experimental spectrum matches those predicted for the C_1 (or C_s) *tert*-butyl cation geometries extremely well. Figure 1 also shows that other skeletal isomers of $C_4H_9^+$ have significantly different spectra, particularly in the position of the main band in the C−H stretching region; this is located further to the red for the *tert*-butyl cation than for any other isomer. The specific pattern of bands in the fingerprint region differ as well. Our results agree with the IR spectra of several $C_4H_9^+$ isomers computed previously by Schleyer's group at a slightly lower level of theory.[6−8] Clearly, the spectrum measured here for $C_4H_9^+$-Ar is due to the *tert*-butyl cation.

Olah and co-workers[2b] reported the infrared spectrum of the *tert*-butyl cation in superacid matrices and noted two important features resulting from charge delocalization and hyperconjugation. The

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Table 1. The IR Bands Observed Compared to Previous Work and to the Predictions of Theory (scaled Frequencies and Intensities in km/mol)

this expt	theory (int)	assignment	Olah et al.
970	936 (39.7)	asym C str/methyl bend	962
1098	1062 (40.6)	sym C str/methyl bend	1070
1278	1253 (68.5)	asym C str/methyl bend	
1302	1283 (98.9)	asym C str/methyl bend	1290
	1291 (20.3)	sym C str/methyl bend	
1316	1325 (130.6)	asym C str/methyl bend	
1410	1380 (8.5)	asym C str/methyl bend	
1465	1445 (5.1)	asym C str/methyl bend	1455
	1446 (20.7)	asym C str/methyl bend	
1476	1459 (24.5)	asym C str/methyl bend	
	2832 (87.0)	asym C−H str	
2834	2833 (119.6)	asym C−H str	2830
	2846 (10.1)	asym C−H str	
2965	2980 (2.1)	asym C−H str	
	2982 (3.4)	asym C−H str	
	2984 (11.4)	asym C−H str	
3036	3055 (3.8)	asym C−H str	
	3059 (2.1)	asym C−H str	
	3064 (3.0)	asym C−H str	

C−H stretching fundamentals occurred at an exceptionally low frequency (2830 cm^{-1}), and the asymmetric carbon stretching vibration frequency was exceptionally high (1290 cm^{-1}). Olah's spectral assignments were validated by the theoretical work of Schleyer et al., which also investigated the $C_4H_9^+$ potential surface and predicted IR spectra for various isomers.[6−8] Our present computations confirm that the *tert*-butyl cation is by far the lowest energy isomer. Possible C_1, C_s, C_{3h}, and C_{3v} t-$C_4H_9^+$ configurations differ in the orientation of the methyl groups. The first three are extremely close in energy, but the C_1 form is the only minimum and is favored by entropy.

The four carbons in all these conformations are essentially coplanar (central C out of the plane of the other three by 0.013 Å), consistent with the sp^2 hybridization of the central carbon. The C_1 (near-C_s) geometry has three hyperconjugatively elongated (to ca. 1.11 Å) C−H bonds aligned parallel to the central carbon p orbital. Two of these C−H bonds are on one side of the carbon plane; the third is on the other. This minimizes the steric crowding of the remaining methyl hydrogens.[6] Hyperconjugation also decreases the CCH bond angles (to ca. 103°) and reduces the C−H stretching frequencies. The charge redistribution and sp^2 hybridization contracts the C−C bonds (1.457 Å; the NMR nutation and X-ray lengths are 1.46[18] and 1.442(5)[5] Å, respectively) and increases their stretching frequencies.

Our gas phase measurements provide a high quality infrared spectrum of the *tert*-butyl cation. Compared to Olah's superacid matrix measurement,[2b] the linewidths, sensitivity, and resolution are much improved. New weaker vibrational bands are detected. The low temperature of the supersonic expansion results in sharper vibrational bands. However, the intensities of our lower frequency bands are depressed relative to the calculated values, presumably because the dissociation efficiency is less at low energy and the laser power is lower here. Although the conditions are quite different between our gas-phase spectrum and Olah's in a superacid matrix, the *band positions* in the two spectra are remarkably similar. Olah's main C−H stretching feature at 2830 cm^{-1} compares to ours at 2834 cm^{-1}, while his asymmetric carbon stretch at 1290 cm^{-1} is now resolved into a triplet of bands at 1278, 1302, and 1316 cm^{-1}. We confirm and extend the previous vibrational assignments (see Table 1). Unlike our mass selected measurements in the gas phase, matrix backgrounds, counterions, or impurities might perturb the *tert*-butyl cation IR spectrum in the superacid matrix. Evidently, this does not occur to a major extent.

Our spectrum also confirms the structure of the *tert*-butyl cation. Hyperconjugative interactions produce the red-shifted C−H stretches, but the methyl group configurations only affect the multiplet near 1300 cm^{-1}, which also is extremely sensitive to the near-planarity of the carbon skeleton. Only the C_1 and C_s configurations match the observed IR patterns. Internal methyl rotation is conceivable, but unlikely. The ion temperature is only 50−100 K, and we estimate the barrier to be 0.5 kcal/mol.

The new gas-phase spectrum confirms the classic picture of the *tert*-butyl cation with its extraordinary stability gained through charge delocalization and hyperconjugation. In conjunction with theoretical computations, we are now using the photodissociation methods described here, employing new infrared lasers and ion sources with supersonic cooling, to probe the structures of a variety of carbocations in the gas phase.

Acknowledgment. This paper is dedicated to George Olah on the occasion of his 80th birthday. We gratefully acknowledge support of this work from National Science Foundation Grants CHE-0551202 and CHE-0716718.

Supporting Information Available: Details on the ab initio calculations for the different isomeric structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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