Ultraviolet Photoelectron Spectroscopy of the *tert*-Butylvinylidene Anion

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The 351 nm photoelectron spectrum of the *tert*-butylvinylidene anion is reported. The electron affinity of the **X** $^1A'$ state of *tert*-butylvinylidene is 0.645(15) eV, and the excitation energy of the $^3A'$ state is 1.975(15) eV. The influence of the *tert*-butyl substituent on the properties of the vinylidene group in the anion, neutral singlet, and neutral triplets is examined by comparing the energetics and vibrational modes apparent in the photoelectron spectrum with those of vinylidene, fluorovinylidene, and vinylvinylidene. The electronic state energetics are found to parallel closely those of unsubstituted vinylidene while the vibrational modes activated by electron detachment from the anion are similar to those of vinylvinylidene; using these findings the term energy of the $^3A''$ state is estimated as 2.45(15) eV. The *tert*-butylvinylidene anion photoelectron spectrum is the first to be analyzed without the aid of explicit high-level ab initio calculations, due to the similarity of vibrational modes to those in the vinylvinylidene spectrum.

Introduction

The 1,2-hydrogen shift rearrangement (eq 1), one of the most

$$\begin{matrix} H \\ \diagdown \\ \quad\quad C=C: \\ \diagup \\ X \end{matrix} \longrightarrow X-C\equiv C-H \qquad (1)$$
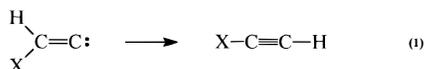
ubiquitous intramolecular reactions, has been studied in some detail both experimentally[1−4] and theoretically.[5−12] The rearrangement of vinylidene (H_2CC) to acetylene is the simplest example of such a rearrangement and has been studied most extensively. The ground singlet state of vinylidene has an empty orbital on the terminal carbon atom to which a hydrogen atom can migrate,[7] making the barrier to rearrangement so small that its existence has been disputed. The anion and the triplet states of the neutral, however, have no such empty orbital so that the CH bond of the migrating hydrogen has to be broken before isomerization can occur, resulting in much larger barriers (40−50 kcal/mol). Calculations of the singlet barrier have a long history, with the first large-scale calculation in 1978 from the Schaefer group,[5] which found a barrier of 5−8 kcal/mol. In 1981, the Schaefer group refined their calculations[9] to provide a barrier of 4 kcal/mol, but other calculations the same year[8] found no barrier at the MP2 and MP4 levels of theory. The most recent calculation,[11] also from the Schaefer group, provides an estimate to the isomerization barrier of 3 kcal/mol.

Two experimental studies of vinylidene which were undertaken in this laboratory[1,2] indicate that the singlet is a true minimum on the potential energy surface based on the observation of distinct vibrational levels in a mode closely resembling the reaction path. The more recent study[1] includes a detailed analysis of the singlet state spectrum aided by ab initio calculations of the vibrational frequencies available to the anion, singlet, and $^3B_2$ states. The CH_2 rock, which would be symmetry forbidden in a harmonic potential, was found to be active in the singlet state spectrum as a result of the significantly anharmonic potential energy surface. This indicates that the CH_2 rock approximates the isomerization coordinate and facilitates an estimate of the minimum well depth as greater than two vibrational levels in the CH_2 rock (450 cm^{-1}, or 1.3 kcal/mol). A small amount of lifetime broadening may also

be present in the singlet spectrum, from which the lifetime of the singlet state (0.04−0.2 ps) and corresponding barrier height to isomerization (∼2 kcal/mol) were estimated. The two studies of the vinylidene anion photoelectron spectrum illustrated the enormous potential of negative ion photoelectron spectroscopy for probing transient species.

The next step in elucidating the properties affecting the 1,2-hydrogen shift was to perturb the system by replacing one or both of the hydrogen atoms in vinylidene with a halogen atom to probe the effect of a much more electronegative substituent without increasing the number of atoms in the system. An experimental study of fluorovinylidene (HFCC$^-$) and difluorovinylidene (F$_2$CC$^-$) anions was performed in this laboratory[3] concurrently with sophisticated calculations by the Schaefer group.[12] The fluorovinylidene anion photoelectron spectrum contains transitions to a singlet ground state and two triplets of fluorovinylidene, similar to the vinylidene case. The photoelectron spectrum showed that the normal coordinate displacement from the anion geometry to the singlet geometry is larger than that for vinylidene, and the calculations showed that the vibrational mode closest to the isomerization coordinate is the CCF bend. Because the spectrum is highly congested and the frequency of the CCF bend is very low (205 cm^{-1}), however, no estimate of the lifetime of the singlet was obtainable. The barrier height to isomerization was estimated as 2 ± 1 kcal/mol by modeling the CCF bend coordinate as a Morse oscillator to estimate the anharmonicity of this mode ($\omega_e x_e = 14$ cm^{-1}). The effect of replacing the hydrogen atoms in vinylidene with fluorine atoms was found to increase the electron affinities (F$_2$CC > HFCC > H$_2$CC) and decrease the singlet−triplet splittings (F$_2$CC < HFCC < H$_2$CC) for both observable triplet states. These observations show that the energy difference between the anion ground state and the triplet states remains nearly constant; this effect is most apparent for the $^3A_2$ (or $^3A''$) state, for which the anion−triplet splitting is 3.244, 3.038, and 3.179 eV for H$_2$CC, HFCC, and F$_2$CC, respectively.

The most recent vinylidene system studied in this laboratory, vinylvinylidene[4] (H$_2$C=CHCH=C$^-$), is well supported by ab initio calculations. The vinylvinylidene anion photoelectron spectrum is remarkably similar to that of vinylidene, despite the presence of a vinyl substituent. Two triplet states and one singlet state of vinylvinylidene appear in the spectrum, and the vibrational peaks are much broader in the singlet than in the


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triplets. The large peak widths (~50 meV) in the singlet state spectrum were found[4] to be due largely to vibrational congestion in the CCC bending vibration, which is shown by the calculations to be close to the isomerization coordinate. Transitions to several vibrational levels (at 360, 500, 835, and 1250 cm^{-1}) of the ^{3}A′ state appear which follow a reasonable Franck–Condon progression, except that the ^{3}A″ state appears as a single, small peak intermingled with the transitions to excited vibrations of the ^{3}A′ state. The electron affinity of vinylvinylidene (0.914 eV) was found to be intermediate between those of vinylidene (0.490 eV) and fluorovinylidene (1.718 eV). The relative order of the two triplet states is the same in vinylvinylidene as in vinylidene, unlike the fluorovinylidene case, and the energy separation between the vinylvinylidene anion ground state and neutral ^{3}A″ state (2.949 eV) was found to be very close to the vinylidene anion ground state to neutral ^{3}A$_2$ energy difference (3.244 eV), continuing the trend found in the HFCC and F$_2$CC cases.

The experimental technique used to obtain the *tert*-butylvinylidene anion photoelectron spectrum will be described briefly. The region of the spectrum corresponding to transitions to the ^{3}A′ state will be discussed before examining the singlet ground state spectrum. The analysis of the *tert*-butylvinylidene anion spectrum and the resulting conclusions rely heavily on comparisons with the negative ion photoelectron spectra of vinylidene and vinylvinylidene, and we will conclude with comments about the features apparently common to the photoelectron spectra of general substituted vinylidene anions.

Experimental Section

The photoelectron spectrometer has been described in detail previously, and so only a brief description of the apparatus will be presented here. The ions are formed in a microwave flowing afterglow by reacting the precursor, 3,3-dimethyl-1-butene, with O$^-$ in a flowing afterglow microwave discharge ion source. The reaction that forms *tert*-butylvinylidene[13] is

$$\underset{(CH_3)_3C}{\overset{H}{\diagdown}}C=CH_2 + O^- \rightarrow \underset{(CH_3)_3C}{\overset{H}{\diagdown}}C=C^{\ominus} + H_2O \qquad (2)$$
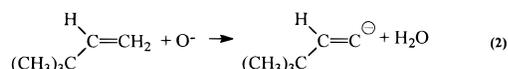
The O$^-$ is formed in a flow of helium (6 standard liters per minute) with O$_2$ (~0.2%) through the microwave discharge, and the 3,3-dimethyl-1-butene is introduced through a downstream inlet. Typical ion beam currents of *tert*-butylvinylidene were 16 pA.

The reaction can be assumed to proceed in this way and not abstract other protons because (1) hydrogens on terminal, unsaturated carbon atoms have been found[13] to be more acidic than methyl group protons, (2) in cases where a vinylidene group is formed, two protons can be abstracted by O$^-$ but only one will not abstract, and (3) the similarity of the photoelectron spectra (to be discussed below) obtained from the product of this reaction at 82 amu to the other vinylidene system spectra obtained in this laboratory forces the conclusion that this also is a vinylidenic system.

Once formed, the ions are accelerated and focused into a Wien mass filter, decelerated, and passed through the focus of a 351 nm laser buildup cavity. Electrons are photodetached by ~75 W of laser light and energy analyzed by a hemispherical electron kinetic energy analyzer equipped with a position-sensitive detector. Typical electron energy resolution is 6 meV. The absolute energy scale is calibrated by measuring the photoelectron spectrum of O$^-$, for which the electron affinity is well-known.[14]
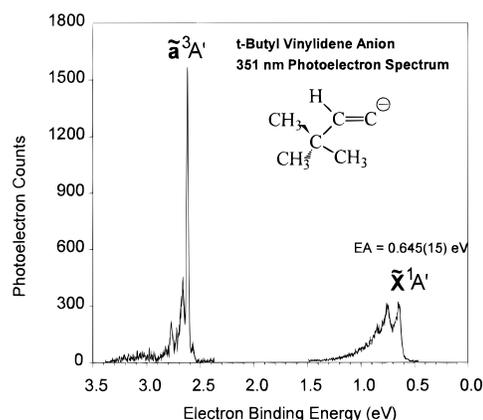

Figure 1. 351 nm photoelectron spectrum of *tert*-butylvinylidene anion. The data are the same as in Figures 2 and 3, with the triplet state region scaled accordingly to represent the appropriate relative cross sections of the singlet and triplet states.
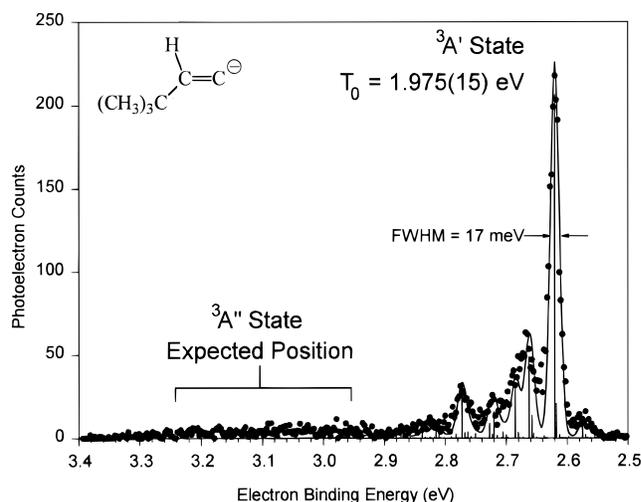

Figure 2. ^{3}A′ state region of the 351 nm photoelectron spectrum of the *tert*-butylvinylidene anion. Symbols represent the experimental data; sticks represent positions and relative intensities of transitions in a Franck–Condon simulation; the solid line represents the same Franck–Condon simulation convoluted with 17 meV Gaussians.

Results and Discussion

The photoelectron spectrum of the *tert*-butylvinylidene anion is presented in Figure 1. The intensity of the high binding energy portion of the spectrum relative to the low binding energy region is approximate, since the two regions were obtained in different scans. The ground state singlet is the lower binding energy signal and has a vibrational origin at 0.645(15) eV binding energy, which corresponds to the electron affinity of *tert*-butylvinylidene. The intense peak at 2.620(6) eV binding energy corresponds to transitions from the anion to the ^{3}A′ state; from this the ^{1}A′ ↔ ^{3}A′ singlet–triplet splitting of *tert*-butylvinylidene is readily found to be 1.975(15) eV. The most obvious difference between the singlet and triplet state spectra, aside from the relative cross sections, is the much greater peak widths in the singlet state spectrum. This difference is due to the excitation of low-frequency vibrational modes in the singlet and, possibly, to the presence of lifetime broadening. In the following, we examine the triplet state spectrum in greater detail before turning to the singlet state spectrum.

Figure 2 depicts the triplet state region of the photoelectron spectrum, from 2.5 to 3.4 eV binding energy. The data are represented by symbols; a Franck–Condon analysis of the spectrum is represented by sticks for the positions and magnitudes of transitions and a line for the simulation convoluted

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TABLE 1: Vibrational Frequencies and Normal Coordinates Measured for the $^3A'$ State of *tert*-Butylvinylidene by Negative Ion Photoelectron Spectroscopy[a]

	vinylvinylidene[b]	*tert*-butylvinylidene	
	vibrational frequency (cm^{-1})	normal coordinate displacement	vibrational frequency (cm^{-1})
anion $^2A'$ state	250(30)		370[c]
neutral $^3A'$ state	360(50)	0.21	340
	500(50)	0.14	520
	835(50)	0.08	800
	1250(50)	0.09	1230

[a] These modes, and only these modes, were observed in the vinylvinylidene $^3A'$ state photoelectron spectrum. [b] In the vinylvinylidene case, no Franck−Condon simulation was attempted due to contamination of the signal by the $^3A''$ state, so no normal coordinate displacements were determined. [c] The 370 cm^{-1} mode in *tert*-butylvinylidene anion is assumed to be the same mode as the 340 cm^{-1} mode in the triplet. All other anion frequencies are held equal to the triplet state frequencies for the Franck−Condon simulation.

with a Gaussian peak (FWHM = 17 meV) for each transition. The vibrationless origin is fixed at 2.620 eV binding energy, and the vibrational frequencies and normal coordinate displacements obtained through the simulation are listed in Table 1. The previously observed vibrational frequencies of the $^3A'$ state of vinylvinylidene are also included for comparison. The frequencies observed in the *tert*-butylvinylidene $^3A'$ state closely match those of vinylvinylidene, indicating that the geometry change between anion and neutral is remarkably similar in both cases. While the normal coordinate displacements for activation of the *tert*-butylvinylidene vibrations are available from the Franck−Condon simulation (Table 1), the vinylvinylidene spectrum is complicated by the presence of a second triplet state ($^3A''$) at ~1000 cm^{-1} higher binding energy than the origin of the $^3A'$ state, making a Franck−Condon analysis difficult. The analogous $^3A''$ state of *tert*-butylvinylidene should be accessible within the electron kinetic energy range of the photoelectron spectrometer; however, no evidence of such a state is apparent in the spectrum. This is not a surprising result since this second triplet state has proven to have a very small cross section for photodetachment in the spectra of all vinylidene anions[1,3,4] investigated to this point. Arguments based on the relative energetics of the anion, singlet, and two triplet states observed in the other vinylidene systems will be presented below that support the expectation for the $^3A''$ state to appear in the range indicated in Figure 2.

With the observation of several vibrational modes in the $^3A'$ state of *tert*-butylvinylidene and one mode in the anion (Table 1), the portion of the photoelectron spectrum of *tert*-butylvinylidene anion shown in Figure 2 has been characterized as well as possible without extensive ab initio calculations. The narrow (17 meV) peak widths of the vibrational levels in this state, and the relatively small measured normal coordinate displacements, are not surprising results given the similar findings presented previously for other vinylidene systems.[1,3,4] Slightly more surprising is the fact that the vibrational modes activated in the *tert*-butylvinylidene $^3A'$ state are **almost identical** to those of the vinylvinylidene $^3A'$ state. The ab initio calculations performed on vinylvinylidene show that the internal structure of the vinyl group is not as important to the isomerization process as its identity as an alkyl substituent. The remarkable similarity between the spectra of *tert*-butylvinylidene and vinylvinylidene indicates that alkyl-substituted vinylidenes in general undergo the same structural changes upon electron detachment from the anions; in other words, the vibrational modes found in the vinylvinylidene and *tert*-butylvinylidene $^3A'$ state spectrum may represent a signature of alkyl-substituted
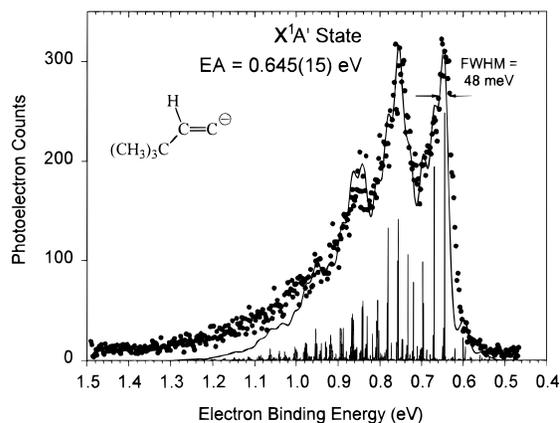

Figure 3. X $^1A'$ state region of the 351 nm photoelectron spectrum of the *tert*-butylvinylidene anion. Symbols represent the experimental data; sticks represent positions and relative intensities of transitions in a Franck−Condon simulation; the solid line represents the same Franck−Condon simulation convoluted with 24 meV Gaussians.

vinylidenes. An analogous signature may be present in the *tert*-butylvinylidene singlet state spectrum presented below. To evaluate this possibility, we draw extensively on our previous investigation of the vinylvinylidene spectrum as a guide to interpreting the *tert*-butylvinylidene singlet state spectrum.

The singlet state region (0.5−1.4 eV binding energy) of the *tert*-butylvinylidene anion photoelectron spectrum is in Figure 3. Superimposed on the spectrum is a Franck−Condon analysis, with sticks representing the positions and relative intensities of individual transitions and a solid line representing the corresponding simulation convoluted with 24 meV FWHM Gaussians. The singlet spectrum exhibits much more vibrational congestion than the triplet spectrum discussed above. The qualitative appearance of the spectrum is not dissimilar from the singlet state spectrum of vinylvinylidene, much as the $^3A'$ state spectra are similar, and this resemblance is used to a great extent for the Franck−Condon simulation. The parameters obtained for the vinylvinylidene singlet, listed in Table 2, were used as a starting point and adjusted in small increments to empirically fit the *tert*-butylvinylidene spectrum. The parameters which correspond to the simulation in Figure 3 are included in Table 2. The adjustments required to arrive at a reasonably satisfactory simulation are relatively small, with the largest adjustments required for some of the normal mode displacements. Also included in Table 2 are the descriptions of the vibrational modes deduced from the ab initio calculations of vinylvinylidene. It is expected that ab initio calculations performed on *tert*-butylvinylidene would yield vibrational frequencies very similar to those listed in Table 2, and the normal mode descriptions of such modes should be analogous to those of the vinylvinylidene singlet. The lowest frequency mode at 200 cm^{-1}, in particular, is probably the closest mode to the isomerization coordinate and, in analogy to vinylvinylidene and fluorovinylidene, is ascribed to the $C_1C_2C_3$ bend (where C_1 is the terminal carbon). The singlet state region of the *tert*-butylvinylidene anion photoelectron spectrum, therefore, is extremely similar to that of the vinylvinylidene anion spectrum. This finding further encourages the conclusion that the photoelectron spectra of alkyl-substituted vinylidene anions contain a common, easily recognizable signature.

This analysis of the *tert*-butylvinylidene anion photoelectron spectrum has relied heavily on the analyses previously presented[1,3,4] for other vinylidene anion spectra. The similarity between the spectrum (Figure 1) and the other vinylidene spectra justifies this procedure. This represents, therefore, the first vinylidene anion system which has been a tractable problem

TABLE 2: Vibrational Frequencies and Normal Coordinates Used in Franck−Condon Simulations of the Negative Ion Photoelectron Spectra of the $^1A'$ States of Vinylvinylidene and *tert*-Butylvinylidene[a]

description	vinylvinylidene		*tert*-butylvinylidene	
	frequency[b] (cm^{-1})	best fit displacement (amu$^{1/2}$ bohr)	frequency (cm^{-1})	best fit displacement (amu$^{1/2}$ bohr)
$C_1C_2C_3$ bend	136	0.708	200	0.40
skeletal rock	413	0.106	413	0.24
C_2C_3 stretch	876	0.128	700	0.20
H_5 rock	915	0.154	880	0.21
H_5/H_6 rock	1126	0.141	1126	0.05
C_1-C_4 antisymmetric stretch	1695	0.063	1600	0.08

[a] Descriptions of the vinylvinylidene modes were obtained by ab initio calculations.[4] *tert*-Butylvinylidene simulation results from adjusting the vinylvinylidene values to fit the *tert*-butylvinylidene spectrum. [b] All vinylvinylidene frequencies are 93% of the CISD calculated values, except the $C_1C_2C_3$ bend which is an empirical adjustment to the calculated frequency.
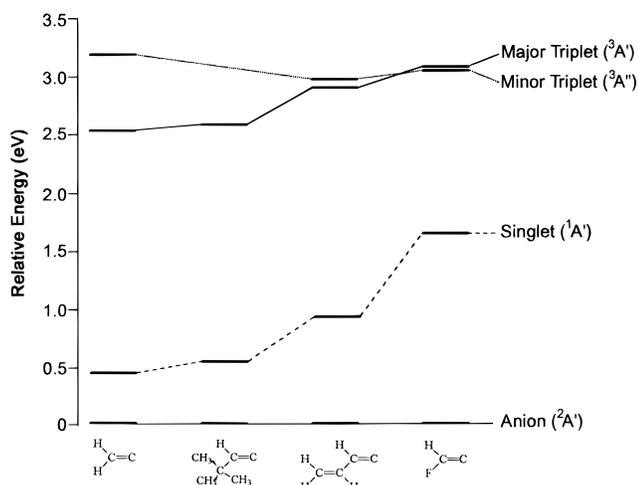

Figure 4. Energies of the anion and neutral states of vinylidene, *tert*-butylvinylidene, vinylvinylidene, and fluorovinylidene, as measured by negative ion photoelectron spectroscopy. The two observable triplet states are denoted "major" and "minor" to indicate their large and small cross sections, respectively, for photodetachment from the anion. The $^3A''$ state of *tert*-butylvinylidene has not been observed and is expected to appear at 3.10(15) eV. Vinylidene data from ref 1; vinylvinylidene from ref 4; fluorovinylidene from ref 3.

without the aid of extensive ab initio calculations. The base of knowledge now available about vinylidenes enables the rapid extraction of some vital properties, including electron affinities, the first two singlet-triplet splittings, relative cross sections of the three electronic states accessible within 3.5 eV binding energy, and some of the vibrational mode excitations.

In the case of *tert*-butylvinylidene, the second triplet state ($^3A''$) is not observed in the negative ion photoelectron spectrum. Its approximate binding energy can be obtained, however, by direct comparison with the other vinylidenes. The energies of the vibrationless origins of the observed electronic states of vinylidene, *tert*-butylvinylidene, vinylvinylidene, and fluorovinylidene, relative to the anions, are reproduced graphically in Figure 4. Moving from left to right in Figure 4, the energies of the singlet state origins (electron affinities) increase dramatically. The binding energies of the $^3A'$ state ($^3B_2$ in vinylidene) increase in an approximately parallel fashion to the singlets, although the change is not as dramatic in this case. The $^3A_2$ state binding energy in vinylidene is 3.244 eV and decreases (as the $^3A''$ state energy) toward the right side of Figure 4, until it is slightly lower than the $^3A'$ state in fluorovinylidene. The trends in the electronic state energies of these species are closely correlated with the electron-withdrawing properties of the substituents, which increase from left to right in Figure 4 (e.g., H < *tert*-butyl < vinyl < F). Furthermore, the energies of the *tert*-butylvinylidene states are nearly equivalent to those of vinylidene and more dramatically different from those of vinylvinylidene.

The expected position of the $^3A''$ state of *tert*-butylvinylidene is apparent from Figure 4: the binding energy should be slightly lower than that of the $^3A_2$ state of vinylidene (3.244 eV) and higher than that of the vinylvinylidene $^3A''$ state (2.949 eV). The expected binding energy of the *tert*-butylvinylidene $^3A''$ state, therefore, is 3.10(15) eV, which can be used with the measured electron affinity (0.645 eV) to yield a $^3A'' \leftrightarrow {}^1A'$ excitation energy of 2.45(15) eV.

Previous investigations into the photoelectron spectra of vinylidenic anions have focused on determining the singlet state lifetime, and in all cases this lifetime has been estimated to be in the range of 20−200 fs. The remarkable similarities apparent in the vibrational analysis of the *tert*-butylvinylidene spectrum to that of vinylvinylidene reflect the corresponding similarity of these potential energy surfaces and provide evidence that the lifetime is also very similar. The lifetime of the singlet state of *tert*-butylvinylidene, therefore, is postulated to be approximately equal to that of vinylvinylidene and therefore also equal, within our experimental resolution, to those of vinylidene and fluorovinylidene.

Conclusion

The photoelectron spectrum of the *tert*-butylvinylidene anion has been measured. The electron affinity of *tert*-butylvinylidene is 0.645(15) eV, and the $^1A' \leftrightarrow {}^3A'$ singlet−triplet splitting is 1.975(15) eV. Four vibrational frequencies of the $^3A'$ state, and one of the $^2A'$ anion ground state, have been measured along with the normal coordinate displacements in these modes. The previously reported analysis of the vinylvinylidene singlet state spectrum has been used successfully as a guide to analyzing that of *tert*-butylvinylidene. The appearance of the *tert*-butylvinylidene anion photoelectron spectrum is remarkably similar to that of the vinylvinylidene anion, except that the electronic state binding energies are closer to those measured in the photoelectron spectrum of the vinylidene anion.

Several features have been identified as common to the photoelectron spectra of the vinylidene, *tert*-butylvinylidene, vinylvinylidene, and fluorovinylidene anions. In addition, striking trends in the electron binding energies of the observable electronic states in these spectra have been identified as correlated with the electron-withdrawing capabilities of the respective substituents. These trends have been used to infer the approximate term energy of the *tert*-butylvinylidene $^3A''$ state, despite its absence in the photoelectron spectrum.

While the electronic state term energies of *tert*-butylvinylidene are most similar to those of vinylidene, the vibrational modes activated by photoelectron detachment from the anion are remarkably similar to those of vinylvinylidene. These facts indicate that, while the electronic state properties of the vinylidene systems are most strongly affected by the electron-withdrawing nature of the substituent, the vibrational modes activated by electron detachment are more closely correlated

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with the mass of the substituent. This indicates that the curvatures of the potential energy surfaces remain fairly constant regardless of the identities of the substituents, even when the relative positions of these surfaces change dramatically.

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