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# Electron Energy Loss Studies of Vibrational and Electronic Excitation Processes in 1,3-Butadiene: The Role of Core-Excited Anion States

**M. F. Falcetta and K. D. Jordan***

*Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260.* *Received February 28, 1991. Revised Manuscript Received June 3, 1991*

**Abstract:** A magnetically collimated electron energy loss spectrometer has been used to determine the electron energy dependence of the cross sections for production of the $1^3B_u$, $1^3A_g$, and $1^1B_u$ excited states as well as for the excitation of 3 quanta of CH stretch and of 3 quanta of C=C stretch in the $^1A_g$ ground state of 1,3-butadiene. These cross sections display peaks due to the two $\pi^*$ anion states as well as to various $\pi^{-1}(\pi^*)^2$ core-excited anion states. Evidence for a broad $\sigma^*$ anion state and for $\pi^{-1}(3s)^2$ and $\pi^{-1}(3p)^2$ Feshbach resonances is presented. Assignments are proposed for the low-lying core-excited anion states.

## I. Introduction

1,3-Butadiene, hereafter referred to simply as butadiene, serves as a paradigm for understanding the electronic structure of "linear" polyenes. A fundamental question concerning polyenes is the validity of molecular orbital (MO) theory for predicting the relative energies of the valence-type states. For an all-trans polyene, the $\pi$ (and $\pi^*$) orbitals alternate, with increasing energy, between $a_u$ and $b_g$ symmetry. It was long believed that the lowest excited singlet state of polyenes would be due to the HOMO → LUMO excitation and, thus, would be of $B_u$ symmetry. However, it is now known that for sufficiently long polyenes the excited $2^1A_g$ state lies energetically below the $1^1B_u$ state.[1] There is evidence that even in butadiene the lowest excited singlet state is $2^1A_g$.[2a,b] However, the assignment in this case is still a matter of debate.[2c,d] Within the MO framework, extensive configuration mixing is required to correctly order the $2^1A_g$ and $1^1B_u$ states.

Early papers discussing the states of the cations[3] and anions[4] of butadiene and other polyenes assumed the approximate validity of Koopmans' theorem[5] (KT), according to which the ionization potentials (IP's) and the electron affinities (EA's) are associated with the negatives of the energies of the filled and unfilled orbitals, respectively. The KT approximation neglects relaxation and correlation effects accompanying electron attachment or electron loss. While the inclusion of relaxation and configuration mixing is clearly required to obtain IP's and EA's in quantitative agreement with experiment, the KT picture has been found to provide a qualitatively correct description of the low-lying states of the ions of many molecules. In recent years several papers have appeared pointing out that configuration mixing may, in fact, be quite important in even the first excited states of the anions and cations of polyenes.[6] This follows from the facts that the lowest energy two-particle-one-hole (2p-1h) configuration of the anion is of the same symmetry as the second unfilled orbital and that the lowest energy one-particle-two-hole (1p-2h) configuration of the cation is of the same symmetry as the second highest occupied $\pi$ orbital. (In this work the "particle" levels are synonymous with the $\pi^*$ orbitals, and the "hole" levels correspond to the $\pi$ orbitals.)

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(1) Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982; Vol. 6, pp 1–95.

(2) (a) Chadwick, R. R.; Gerrity, D. P.; Hudson, B. S. *Chem. Phys. Lett.* **1985**, *115*, 24. (b) Staley, S. W.; Moore, J. H.; Sato, Y. Private communication. (c) Cave, R. J.; Davidson, E. R. *J. Phys. Chem.* **1987**, *91*, 4481. (d) McDiarmid, R. *Int. J. Quantum Chem.* **1986**, *29*, 875.

(3) Brogli, F.; Heilbronner, E. *Theor. Chim. Acta* **1972**, *26*, 289. Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.

(4) Shida, T.; Hamill, W. H. *J. Am. Chem. Soc.* **1966**, *88*, 5371.

(5) Koopmans, T. *Physica* **1934**, *1*, 104.

(6) (a) Bally, T.; Nitsche, S.; Kuno, R.; Haselbach, E. *J. Am. Chem. Soc.* **1984**, *106*, 104. (b) Herriok, D. R. *J. Chem. Phys.* **1981**, *74*, 1293. (c) Schulz, R.; Schweig, A.; Zittlau, W. *J. Am. Chem. Soc.* **1983**, *105*, 2980. (d) Cederbaum, L. S.; Domcke, W.; Shirmer, J.; Von Niessen, W.; Dickersen, G. H. F.; Kraemer, W. P. *J. Chem. Phys.* **1978**, *69*, 1591. (e) Koenig, T.; Klopfenstein, C. E.; Southworth, S.; Hoobler, J. A.; Wielesek, R. A.; Balle, T.; Snell, W.; Imre, D. *J. Am. Chem. Soc.* **1983**, *105*, 2256.

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Because polyenes are alternant hydrocarbons, there is a pairing between their anion and cation states as described by Hückel and PPP Hamiltonians.[7] While pairing is not a property of the full electronic Hamiltonian, it should still be qualitatively useful in comparing the trends in the anion and cation states. In particular, the degree of configuration mixing is expected to be roughly comparable in an anion state and the cation state with which it is paired.

Configuration mixing is relatively unimportant for the ground-state cation ($1^2B_g$) or anion ($1^2A_u$) of butadiene. On the other hand, as noted above, sizable configuration mixing might be expected in the lowest excited states of the ions. For example, PPP–CI calculations, of Bally et al., predict that the 1h (KT) and (1p-2h) configurations enter with significant weights in the wave functions of both the $1^2A_u$ and $2^2A_u$ cation states of butadiene.[6] Other researchers, using other semiempirical and ab initio methods, have predicted that the lowest excited cation state of butadiene should be about 20% 1p-2h in character.[8] A similar breakdown of the orbital picture is expected for the first excited ($^2B_g$) temporary anion state, for which the mixing would be between 1p and 2p-1h configurations.

The principal techniques for characterizing gas-phase cations and anions have been photoelectron spectroscopy (PES) and electron transmission spectroscopy (ETS), respectively. In the photoelectron literature, cation states dominated by 1p-2h configurations are called shake-up states, and in the electron scattering field, anion states dominated by 2p-1h configurations are called core-excited resonances. Relatively little experimental data exist on the 2p-1h anion and 1p-2h cation states of butadiene and other polyenes. In part, this is because such states generally appear as relatively weak features in electron transmission and photoelectron spectra, respectively. Another complication is that the 1p-2h cation states generally fall in the same region of the photoelectron spectrum as do cation states because of ionization from high-lying $\sigma$ orbitals. Likewise, the 2p-1h anion states are expected to fall in the same region of the spectra as the $\sigma^*$ anion states. The overlapping of the two types of states should be less problematical in the anion case, since, in the gas phase, $\sigma^*$ anion states have very short lifetimes and tend to be much broader than core-excited anion states, making it relatively easy to distinguish these two types of anion states.

An alternative approach to characterizing the excited states of ions has been to obtain the absorption spectrum of the ground-state radical cation or anion (usually in a matrix). A subset of the 1p-2h cation and 2p-1h anion states can be reached by single electron excitation from the ground-state ion. Of these, those for which the transitions are dipole (and spin) allowed can appear prominently in the absorption spectra.[6] On the other hand, in highly symmetric molecules the transitions to many of the 1p-2h or 2p-1h states of the ions are dipole forbidden.

For the anion states of butadiene, the data available from ETS measurements and absorption studies of the ground-state anion appear not to be fully consistent. The ET measurements of Burrow et al. locate the $1^2A_u$ and $1^2B_g$ anion states at 0.62 and 2.8 eV, respectively.[9] In the simple MO picture, the 0.62- and 2.8-eV anion states are ascribed to 1p states (or shape resonances). The ET spectrum also has a broad, weak feature near 5 eV, which was not assigned by Burrow et al., but is likely due to one or more 2p-1h states. Based on the ET results, the electronic transitions from the ground anion state should occur near 2.2 and 4.4 eV.

An absorption spectrum of the butadiene radical anion in a glassy medium at low temperature displayed intense maxima at 2.2 and 3.2 eV, which were interpreted as arising from the $1^2A_u \rightarrow 1^2B_g$ and $1^2A_u \rightarrow 2^2B_g$ transitions, respectively.[4] The lower transition was attributed to a $2a_u(\pi^*) \rightarrow 2b_g(\pi^*)$ orbital excitation and the upper to a $1b_g(\pi) \rightarrow 2a_u(\pi^*)$ excitation. The lowest transition energy deduced from the ET results is in excellent agreement with that found in the condensed-phase absorption spectrum. However, the condensed-phase measurements give an energy for the second transition about 1.2 eV smaller than that deduced from the ET measurements. There are at least three possible interpretations of these results. Firstly, the second feature in the condensed-phase spectrum may, in fact, be due to the same electronic state as that responsible for the 5-eV feature in the ET spectrum, but shifted due to the fact that the ET experiment probes the anions at the geometry of the neutral molecule, while the absorption spectra probe the excited state anions at the geometry of the ground-state anion. If the geometries of th $1^2A_u$ and $2^2B_g$ anions were to differ sufficiently from each other and from that of the $X^1A_g$ state of the neutral molecule, the two experiments could give very different transition energies. Secondly, even in the absence of a shift in the energy due to differences in the geometries of the various states, it is possible that the energy of the $2^2B_g$ anion state (relative to that of the $1^2A_u$ state) is quite different in the gas phase than in solution. Anion states often have much shorter lifetimes in the gas phase than in the condensed phase, and this can lead to different energies in the two situations.[10] Also, because the anion wave functions tend to be more diffuse for an isolated molecule than in the condensed phase, the extent of configuration mixing may differ in the two cases. Thirdly, it is possible that the 5-eV anion-state feature seen in the ET spectrum is due to a state other than the $2^2B_g$ state, and that the $2^2B_g$ state does indeed lie about 1 eV lower in energy, but is too weak to be seen in the ET spectrum.

In the present study the technique of electron energy loss spectroscopy is used to characterize the various anion states of butadiene. This method is ideally suited for locating and characterizing anion states with considerable 2p-1h character. Such states can be viewed as arising from the attachment of electrons to electronically excited states of the neutral molecule (called parent states). Two-particle-one-hole anion states tend to lie energetically above their parent states owing to the large repulsion between the two electrons in the normally unoccupied valence orbitals. Such 2p-1h states, called core-excited shape resonances,[11] decay strongly back to their parent states, and are manifested as resonances in the cross sections for producing the various excited valence states of the neutral molecule. The importance of this process has been nicely illustrated by Allan[12] in studies of the electron impact excitation of benzene.

Core-excited resonances which lie energetically below their parent states are called Feshbach resonances.[11] Feshbach resonances generally have relatively long lifetimes ($\tau \approx 10^{-13}$ s) since their decay to lower lying states of the neutral molecule occurs via two-electron processes. Feshbach resonances generally involve Rydberg orbitals and have configurations such as $\pi^{-1}(3s)^2$ or $\pi^{-1}(3p)^2$.

## II. Experimental and Theoretical Methods

The electron energy loss spectrometer is similar in design to that of Allan[12] and is only briefly described here. The apparatus uses a trochoidal analyzer[13] to generate an electron beam (1–3nA and 30–60 meV full-width-at-half-maximum) and a dual stage trochoidal analyzer to determine the energies of the electrons scattered in the forward direction. The instrument is immersed in by an axial magnetic field of approximately 80 G. The scattered electrons are detected by means of two microchannel plates in a Chevron arrangement, and the pulses are counted on an Apple IIe microcomputer.

The transmission function of the trochoidal analyzer decreases with residual electron energy ($E_r$) approximately as $1/E_r$.[12] All spectra that involve a variation of the residual energy are corrected by multiplying the signal (at each $E_r$) by $E_r$. The spectra are also corrected by subtracting background counts obtained in the absence of butadiene. An overall resolution of better than 50 meV can be obtained, but most spectra reported here were obtained with approximately 70-meV resolution to reduce the counting times. Even so, counting times of up to 8 h were required to obtain spectra covering an energy range of 10 eV. The

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(7) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; Benjamin: New York, 1966.

(8) See ref 6 for a tabulation of the results of various methods.

(9) Burrow, P. D.; Jordan, K. D. *Chem. Phys. Lett.* **1975**, *36*, 594. See also: Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, *87*, 557.

(10) Jordan, K. D.; Burrow, P. D. *Chem. Phys.* **1980**, *45*, 171.

(11) Schulz, G. *J. Rev. Mod. Phys.* **1973**, *45*, 378.

(12) Allan, M. *J. Electron Spectrosc. Relat. Phenom.* **1989**, *48*, 219.

(13) Stamatovic, A.; Schulz, G. *J. Rev. Sci. Instrum.* **1970**, *41*, 423.

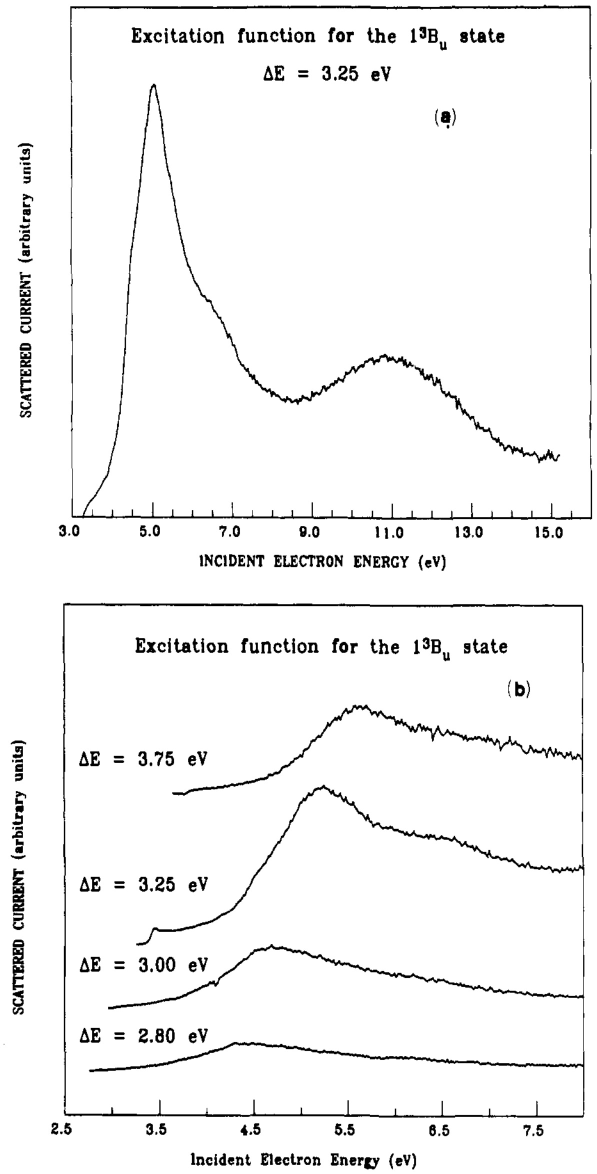

**Figure 1.** Cross section for the production of the $1^3B_u$ state at (a) an energy loss of 3.25 eV, and (b) energy losses of 2.8, 3.0, 3.25, and 3.75 eV.

incident energy scale was calibrated using the onset of the electron beam as zero electron energy, and the energy loss scale was calibrated on the sharp 7.068-eV Rydberg transition of butadiene.[14] Both of these calibrations are expected to be good to 30 meV.

To aid in the assignments, multi-reference configuration interaction (CI) calculations were performed on the cation states. To the extent thatthe pairing theorem holds, the calculations on the cation states are expected to give correct relative energies for the anion states. The calculations were performed on the cation states rather than on the anion states to avoid the computational difficulties presented by the fact that temporary anion states lie in the continuum for electron-molecule scattering.[15]

The calculations on both the $^2B_g$ and $^2A_u$ cation states used 10 reference configurations. The reference spaces consisted of all configurations of either $^2B_g$ or $^2A_u$ symmetry that can be generated by distributing three electrons in the $1a_u$, $1b_g$, $2a_u$, $2b_g$ orbital space. All single and double excitations of the correct spatial symmetry were then generated from the 10 $^2B_g$ or the 10 $^2A_u$ reference configurations, with the restrictions that (1) only single excitations were allowed from the $\sigma$ orbitals, and (2) the eight highest and the eight lowest energy molecular orbitals were kept frozen. The CI calculations were carried out using Hartree-Fock orbitals for the $^2B_g(^1a_u{}^21b_g)$ and $^2A_u(1a_u1b_g{}^2)$ cation states. All calculations employed the 6-31G basis set. The integrals were calculated using the ARGOS program,[16] and the CI calculations were carried out using the programs of Lishka et al.[16] Unless otherwise indicated, the calculations were performed at the experimentally determined geometry of *trans*-1,3-butadiene.[17]

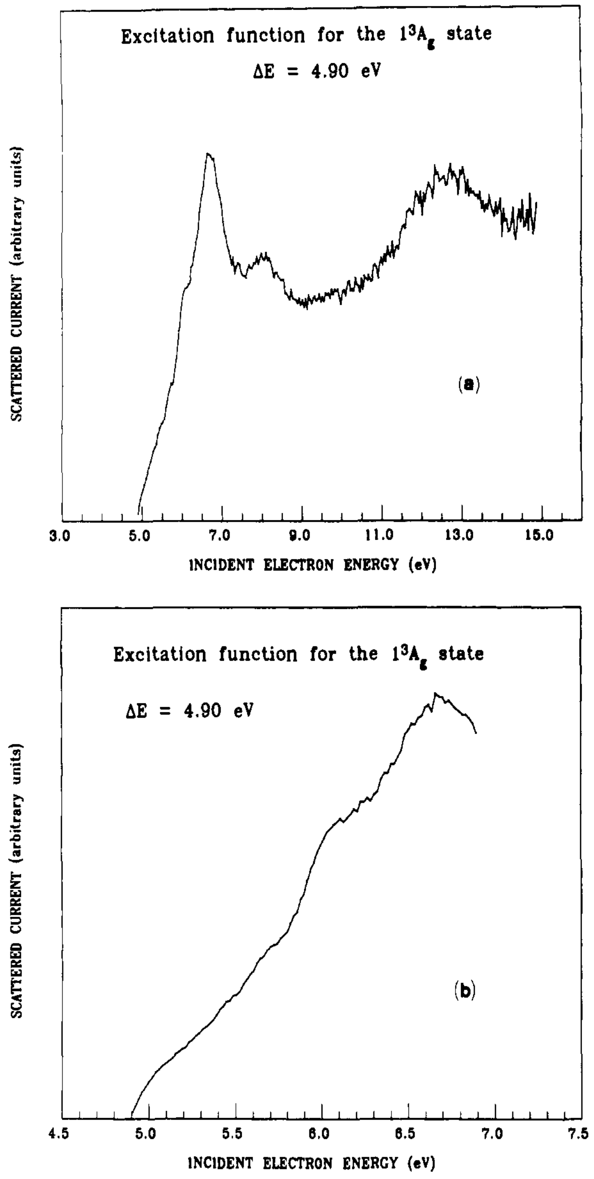

**Figure 2.** Cross section for the production of the $1^3A_g$ state at (a) an energy loss of 4.90 eV, and (b) an energy loss of 4.90 eV, taken with an extended counting time and shown on an expanded scale.

## III. Results and Discussion

**a. Energy Dependence Spectra.** In the absence of any enhancement due to temporary anion formation, triplet states are expected to be excited most strongly at electron energies slightly above threshold, with the excitation probability falling off relatively rapidly with increasing energy; the excitation of a dipole-allowed

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[14] Reddish, T.; Wallbank, B.; Comer, J. *Chem. Phys.* **1986**, *108*, 159.

[15] Because temporary anions lie in the continuum for electron-molecule scattering, commonly used variational methods may converge to states that describe the neutral molecule plus a free electron. One approach to carrying out calculations on such states is the stabilization method. See: Chao, J. S.-Y.; Falcetta, M. F.; Jordan, K. D. *J. Chem. Phys.* **1990**, *93*, 1125 and references therein.

[16] The orbitals used in the CI calculations were obtained by using the MCSCF program of Shepard et al.: Shepard, R.; Simons, J.; Shavitt, I. *J. Chem. Phys.* **1982**, *76*, 543. The program used to perform the CI calculations is described in: Lishka, H.; Shepard, R.; Shavitt, I. *Int. J. Quantum Chem. Symp.* **1981**, *15*, 91. The CI and MCSCF calculations used integrals over symmetry-adapted contracted Gaussian-type orbitals evaluated using the ARGOS program of R. Pitzer. These programs were adapted to the Model FPS 500EA computer by N. Nystrom.

[17] Kuchifsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1967**, *1*, 463.

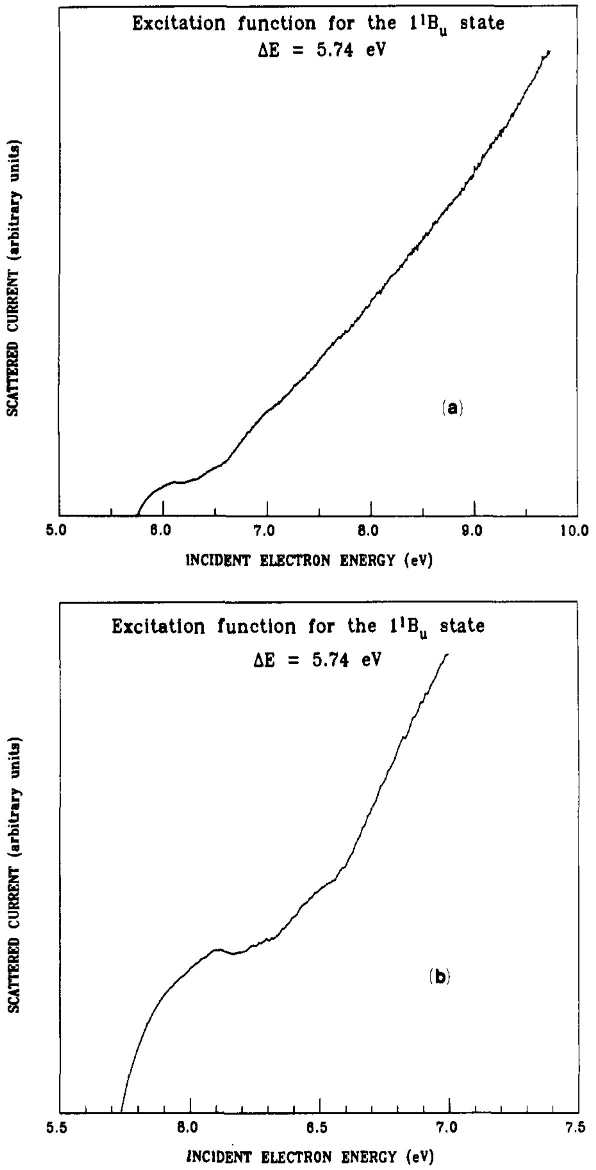

**Figure 3.** Cross section for the production of the $1^1B_u$ state at (a) an energy loss of 5.74 eV, and (b) an energy loss of 5.74 eV, shown on an expanded scale.

singlet state is expected to increase rapidly as electron energy is increased above the threshold value up to some maximum and then to begin to decrease at higher electron energies.[18]

The excitation functions for the $1^3B_u$, $1^3A_g$, and $1^1B_u$ states of butadiene are shown in Figures 1a, 2a, and 3a, respectively. For the $1^3B_u$ and $1^3A_g$ states the spectra have been run with energy losses corresponding to the known vertical transition energies of 3.25 and 4.90 eV, respectively. For the $1^1B_u$ state the energy loss (5.74 eV) has been chosen to correspond to the known transition energy between the vibrational zero-point level of the ground state and the vibrational zero-point level of the $1^1B_u$ state.[14]

The excitation function for the $1^3B_u$ state has a pronounced peak near 5 eV, with a shoulder appearing near 6.6 eV, and a broad peak centered around 11 eV. In order to gain insight into the dependence of the excitation cross section on the energy loss, spectra have also been obtained for energy losses of 2.8, 3.0, and 3.75 eV. The lowest energy loss value of 2.8 eV is close to the adiabatic excitation energy of the $1^3B_u$ state, while the 3.75-eV value is well above the vertical excitation energy. These spectra and the 3.25-eV energy loss spectra are compared in Figure 1b. From Figure 1b it is seen that the maximum in the excitation function shifts from 4.3 eV for an energy loss of 2.8 eV to 5.4 eV for an energy loss of 3.6 eV.

The excitation function for the $1^3A_g$ state, shown in Figure 2a, has maxima near 6.7, 8.0, and 12.5 eV and very weak shoulders near 5.5, 5.7, 6.0, and 6.2 eV. The low-energy portion of the $1^3A_g$ excitation function was rerun with a longer counting time, and the spectrum is shown on an expanded scale in Figure 2b. From the expanded spectrum, the energies of weak shoulders are determined to be 5.45, 5.70, 6.05, and 6.22 eV. There also appears to be still another weak feature near 6.35 eV.

The excitation function for the $1^1B_u$ state, shown in Figure 3a, increases from threshold to about 6.1 eV, levels off for a few tenths of an electron volt, and then increases nearly linearly up to 10.5 eV. Superimposed on the linearly increasing signal are small enhancements near 6.1, 6.5, and 6.9 eV. The structure in the $1^1B_u$ excitation function in the 5.7–7.0-eV range is shown in an expanded scale in Figure 3b, from which it is seen that there is a very weak enhancement near 6.3 eV as well as the previously mentioned enhancements near 6.1 and 6.5 eV.

Resonances with appreciable single-particle character are expected to decay strongly to the $1^1A_g$ ground state. To examine this possibility the instrument was tuned to determine the cross sections for excitation of 3 quanta of symmetric C=C stretch ($3\nu_4$, energy loss of 0.60 eV) and of 3 quanta of CH stretch ($3\nu_1$, energy loss of 1.12 eV).[18] While it would have been desirable to obtain the cross sections for excitation of 1 quanta of $\nu_1$ and 1 quanta of $\nu_4$, this was not done because it is very difficult to tune the apparatus to study processes with energy losses of less than about 0.5 eV. Examination of the fundamental vibrational frequencies of butadiene reveals that the 0.60- and 1.12-eV energy loss processes may arise from various combinations of other fundamentals in addition to the 3 quanta of C=C stretch and 3 quanta of CH stretch mentioned above.

The 0.60- and 1.12-eV excitation spectra, shown in Figure 4, a and b, respectively, both have broad features centered near 4.5 and 8 eV, a series of very weak, narrow features between 2 and 3 eV, and pronounced, narrow features peaking somewhat above threshold. It also appears that there may be a weak, broad feature near 6.5 eV, strongly overlapped by the 4.5- and 8-eV features. The 0.60-eV energy loss spectrum also has a shoulder displaced about 0.20 eV to higher energy from the threshold peak, and a broad, weak feature centered near 2.8 eV. The narrow structures occurring between 2 and 3 eV in both spectra are due to an $N_2$ impurity. The spacing of this structure in the 0.60-eV energy loss spectrum is identical with that for the excitation of $v = 2$ of $N_2$, and that in the 1.12-eV excitation spectrum is identical with that for excitation of $v = 4$ of $N_2$.

**b. Assignments of the Anion States.** The energies of the lowest 10 anion states obtained from the CI calculations along with the dominant configurations involved in each state are presented in Table I. As mentioned previously, the calculations were actually performed on the cation states. The energies of the anion states have been obtained by normalizing the ground-state anion to the experimental attachment energy of 0.62 eV and by using the excitation energies derived from the CI calculations to determine the energies of the other anion states. Figure 5 compares the experimental and theoretical data, showing the energies of the pronounced features in the energy dependence spectra, their decay channels, and the energies of the anion states derived from the CI calculations.

The $1^2A_u$ (0.62 eV) and $1^2B_g$ (2.8 eV) anion states lie energetically below the various electronically excited states of the neutral molecule and, thus, cannot be detected in the excitation functions of these states. The prominent peaks appearing somewhat above threshold in the $3\nu_1$ (1.12 eV) and $3\nu_4$ (0.60 eV) excitation functions are attributed to the $1^2A_u$ anion state, which in the ET spectrum has a vibrational progression in the $\nu_4$ C=C stretch mode extending from 0.62 to 1.20 eV.[9] In the 0.60-eV energy loss spectrum the main peak due to the $1^2A_u$ anion state appears at 0.90 eV, accompanied by a weak shoulder at about 1.10 eV. These two features appear about 0.3 eV higher in energy than the $v = 0$ and $v = 1$ $\nu_4$ levels in the $1^2A_u$ anion as detected

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[18] Panchenko, Y. N. *Spectrochim. Acta* **1975**, *31A*, 1201.

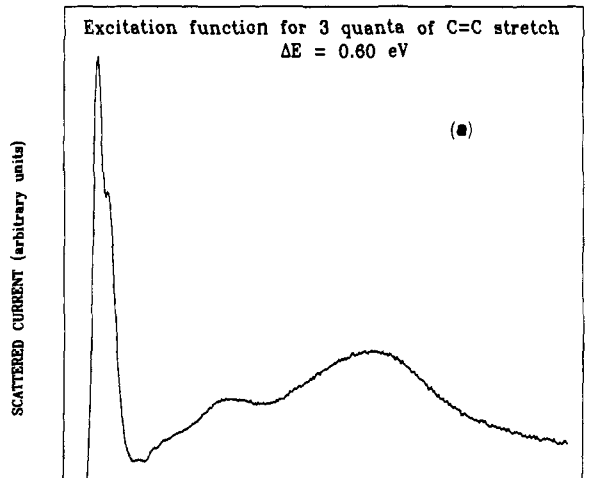

**Figure 4.** Cross sections for production of vibrationally excited levels of the $1^1A_g$ state (a) 3 quanta of $\nu_4$, energy loss of 0.60 eV and (b) 3 quanta of $\nu_1$, energy loss of 1.12 eV.

in the ET spectrum, and could be due either to the $v = 0$ and $v = 1$ levels or to the $v = 1$ and $v = 2$ levels of the $\nu_4$ mode. While the latter interpretation would appear more likely on energetic grounds, the former possibility is suggested by the fact that the structure due to nuclear motion in temporary anions, with lifetimes of the order of a vibrational period, tends to shift to higher energy upon decay into progressively higher vibrational levels of the neutral molecule.[11]

The weak shoulder near 2.8 eV in the 0.60-eV energy loss spectrum is attributed to the $1^2B_g$ anion state, which also appears near 2.8 eV in the ET spectrum. Since the $1^2B_g$ state is expected to have significant single-particle character, one might have expected it to appear more prominently in the $3\nu_1$ excitation spectrum. On the other hand, its weak appearance in the $3\nu_1$ excitation cross section could be due to the fact that there is little distortion along the $v_1$ coordinate during the short lifetime of this anion state.

According to the CI calculations, the $1a_u^2 1b_g^2 2a_u$ configuration enters the $1^2A_u$ wave function with a weight of 0.96, indicating that this state is predominantly 1p in character. On the other hand, two configurations, $1a_u^2 2b_g^2 2b_g$ (0.88) and $1a_u^2 1b_g 2a_u^2$ (−0.35), are particularly important for the $1^2B_g$ state. (The CI coefficients are indicated in parentheses.) These two configurations are also the dominant configurations in the wave function for the $2^2B_g$ state, with coefficients of 0.35 and 0.83, respectively. These results indicate, in accord with previous theoretical studies,[6] that the lowest energy 1p and 2p-1h configurations of $B_g$ symmetry appear prominently in both the $1^2B_g$ and $2^2B_g$ states. The CI calculations also indicate sizable contributions from the $1a_u^2 1b_g 2b_g^2$ (−0.24) and $1a_u 1b_g^2 2a_u 2b_g$ (0.23) configurations in the $2^2B_g$ state.

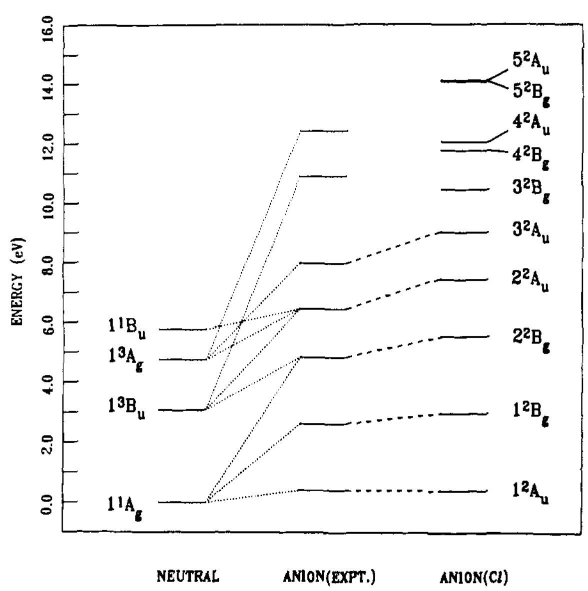

**Figure 5.** Correlation diagram showing the experimentally determined energies of the negative ion states [center column, labeled ANION-(EXPT.)] and the states of the neutral butadiene molecule (left column, labeled NEUTRAL) into which they decay. The right column, labeled ANION(CL), gives the results of the CL calculations for the various anion states.

The CI calculations consistently place the anion states with considerable 2p-1h character about 1 eV too high in energy relative to the $1^2A_u$ ground-state anion. Since they also predict an excitation energy to the lowest 1p-2h cation state about 1 eV higher than that observed experimentally, it would appear that the tendency to place the 1p-2h and 2p-1h states too high in energy derives from basis set deficiencies.

The $2^2B_g$ anion state is predicted to lie near 5.7 eV and is the lowest energy state with predominantly 2p-1h character. Hence, we assign the anion state observed near 5 eV in both the ET and $1^3B_u$ excitation spectra, and near 4.5 eV in the 0.60- and 1.12-eV energy loss spectra, to the $2^2B_g$ state. Since the dominant configuration in the wave function for the $2^2B_g$ anion state is $1a_u^2 1b_g 2a_u^2$, this anion state should decay with a high probability into the $1^3B_u$ state, as is found to be the case. In addition, the importance of the $1a_u^2 1b_g^2 2b_g$ and $1a_u 1b_g^2 2a_u 2b_g$ configurations in the $2^2B_g$ wave function should lead to decay into the $1^3A_g$ state just above threshold, and it is possible that the $1^3A_g$ excitation near 5 eV is enhanced by this process. The sizable coefficient of the $1a_u^2 1b_g^2 2b_g$ configuration in the wave function for the $2^2B_g$ anion state is also consistent with appearance of this anion in the ET spectrum and in the cross sections for exciting various vibrational levels of the $^1A_g$ ground state.

It was noted in the preceding section that the maximum in the $1^3B_u$ excitation function shifts from 4.3 to 5.4 eV as the energy loss increases from 2.8 to 3.75 eV. This trend is consistent with a displacement to longer distances (along some coordinate, e.g., the C=C stretch) as one progresses from the $1^1A_g$ state to the $2^2B_g$ anion state to the $1^3B_u$ state. It is also possible that part of the shift in the peak due to the $2^2B_g$ anion state is due to lifetime effects. Lifetime effects could also be responsible for the appearance of the $2^2B_g$ anion state at lower energies in the vibrational excitation cross sections than in the $1^3B_u$ and $1^3A_g$ excitation functions.

The feature centered at 6.6 eV in the $1^3B_u$ and $1^3A_g$ excitation functions is attributed to the $2^2A_u$ state, which is almost entirely 2p-1h in character and which is predicted in the CI calculations to lie near 7.6 eV. The dominant configurations in the CI wave function for this anion state are $1a_u 1b_g^2 2a_u^2$ (0.74), $1a_u^2 1b_g 2a_u 2b_g$

**Table I.** Energies (eV) and Wave Functions of the $^2A_u$ and $^2B_g$ Anion States As Predicted from CI Calculations[a]

| configurations | energies and CI coefficients for various states | | | | |
|---|---|---|---|---|---|
| | $1^2A_u$ (0.62) | $2^2A_u$ (7.57) | $3^2A_u$ (9.13) | $4^2A_u$ (12.15) | $5^2A_u$ (14.17) |
| $1a_u^2 1b_g^2 2a_u$ | 0.96 | | | | |
| $1a_u^2 1b_g 2a_u 2b_g$[b] | 0.10 | −0.54 | | 0.73 | 0.10 |
| $1a_u 1b_g^2 2a_u^2$ | | 0.74 | −0.23 | 0.45 | 0.26 |
| $1a_u 1b_g^2 2b_g^2$ | | −0.23 | −0.23 | −0.36 | 0.53 |
| $1a_u 1b_g 2a_u^2 2b_g$[b] | | −0.16 | | 0.15 | |
| $1a_u^2 1b_g 2a_u 2b_g$[c] | | 0.10 | 0.86 | | |
| $1a_u^2 2a_u 2b_g^2$ | | | 0.18 | | 0.50 |
| $1a_u 2a_u^2 2b_g^2$ | | | −0.12 | | 0.12 |
| $1a_u 1b_g 2a_u^2 2b_g$[c] | | | −0.11 | | −0.49 |
| $1a_u^2 2a_u 2b_g^2$ | | | | | −0.17 |
| | $1^2B_g$ (3.16) | $2^2B_g$ (5.69) | $3^2B_g$ (10.56) | $4^2B_g$ (11.86) | $5^2B_g$ (14.14) |
| $1a_u^2 1b_g^2 2b_g$ | 0.88 | 0.35 | | | |
| $1a_u^2 1b_g 2a_u^2$ | −0.34 | 0.83 | −0.23 | 0.12 | |
| $1a_u^2 2a_u^2 2b_g$ | −0.16 | | 0.25 | −0.55 | 0.44 |
| $1a_u 1b_g^2 2a_u 2b_g$[b] | −0.10 | 0.23 | 0.24 | −0.58 | −0.55 |
| $1a_u^2 1b_g 2b_g^2$ | | −0.24 | −0.64 | −0.26 | −0.39 |
| $1a_u 1b_g^2 2a_u 2b_g$[c] | | | −0.56 | −0.27 | 0.43 |
| $1b_g 2a_u^2 2b_g^2$ | | | 0.10 | | |
| $1b_g^2 2a_u^2 2b_g$ | | | | 0.25 | −0.14 |
| $1a_u 1b_g 2a_u 2b_g^2$[c] | | | | −0.18 | 0.17 |

[a] The energies of the anion states, given in parentheses, have been adjusted so that the energy of the $1^2A_u$ state agrees with the experimental value. Only the CI coefficients greater than or equal in 0.10 in magnitude have been included. [b] These configurations have the first two unpaired electrons singlet coupled. [c] These configurations have the first two unpaired electrons triplet coupled.

(−0.54), and $1a_u 1b_g^2 2b_g^2$ (−0.23). Given the makeup of this state, it would be expected to decay strongly into both the $1^3A_g$ and $1^3B_u$ states, as is found to be the case. The $2^2A_u$ anion state should also be able to decay into the $1^1B_u$ state (due to the importance of the $1a_u^2 1b_g 2a_u 2b_g$ configuration) and may be responsible for the small enhancement in the $1^1B_u$ cross section near 6.5 eV. It may also be responsible for the weak shoulders near 6.5 eV in the 0.60- and 1.12-eV energy loss spectra. Such a decay process could arise from either (or both) the presence of a small component of the $1a_u^2 1b_g^2 2a_u$ (−0.06) configuration in the $2^2A_u$ anion or configuration mixing in the $1^1A_g$ ground state.

The 8.1-eV anion state, appearing in the $1^3A_g$ excitation cross section, is assigned to the $3^2A_u$ state, which is predicted to fall near 9 eV in the CI calculations. The wave function for the $3^2A_u$ state is dominated by four configurations: $1a_u^2 1b_g 2a_u 2b_g$ (0.86), $1a_u 1b_g^2 2b_g^2$ (−0.23), $1a_u 1b_g^2 2a_u^2$ (−0.23), and $1a_u^2 2a_u 2b_g^2$ (0.18). Although the $3^2A_u$ anion state should also decay strongly to the $1^3B_u$ state of the neutral molecule, the $1^3B_u$ excitation cross section does not show a peak near 8 eV. However, a small peak in this decay channel could be obscured by the broad overlapping features centered at 6.5 and 11 eV. The 11-eV feature in the $1^3B_u$ excitation cross section and the 12-eV feature in the $1^3A_g$ cross section have widths on the order of 4 eV and may each be due to two or more overlapping core-excited anion states.

The feature centered around 8 eV in the 0.60- and 1.12-eV energy loss spectra has a width (ca. 5 eV) appreciably greater than that of the 8-eV feature seen in the cross section for excitation of the $1^3A_g$ state and is likely due to one or more $\sigma^*$ shape resonances. Energy loss studies of other molecules have shown that $\sigma^*$ shape resonances tend to have very large widths and to decay into vibrationally excited levels of the ground state of the neutral molecule.[12]

We now turn our attention to the relatively narrow, weak features which are seen near 6.1 and 6.3 eV in the cross sections for excitation of the $1^1B_u$ and $1^3A_g$ states and near 5.5 and 5.7 eV in the excitation function of the $1^3A_g$ state. These features do not correlate well with any of the calculated valence states of the anion. They could possibly be due to Feshbach resonances, which often lie about 0.5 eV below their parent Rydberg states.[19] The singlet $\pi^{-1}(3s)$ $B_g$ and $\pi^{-1}(3p)$ $A_u$ Rydberg states lie near 6.2 and 7.07 eV, respectively.[14] Electron impact studies of other researchers[14,20] also provide evidence for a Rydberg state near 6.66 eV, which is likely due to another of the $\pi^{-1}(3p)$ Rydberg states. We tentatively assign the 5.5- and 5.7-eV features seen in the $1^3A_g$ excitation function to the $\pi^{-1}(3s)^2$ Feshbach resonance in its zero-point level and with excitation of 1 quanta of C=C stretch, respectively. It is possible that the features seen near 6.1 and 6.3 eV in the $1^3A_g$ as well as the $1^1B_u$ excitation functions are also due to higher vibrational levels in the $\pi^{-1}(3s)^2$ anion state. Alternatively, they could be due to a $\pi^{-1}(3p)^2$ Feshbach resonance as could the weak features near 6.5 and 6.9 eV in the $1^1B_u$ excitation cross section.

**c. Energies of the $2^2B_g$ State in the Condensed and Gas Phase.** In the Introduction it was noted that the absorption spectrum of the radical anion in organic glasses places the $1^2A_u \rightarrow 2^2B_g$ transition at 3.2 eV. The present study shows that in the gas phase the $2^2B_g$ anion state lies about 5 eV above the ground state of the neutral molecule, and about 4.4 eV above the $1^2A_u$ ground-state anion. The difference in the $1^2A_u \rightarrow 2^2B_g$ energies deduced from the gas-phase and condensed-phase studies could be due in part to the different geometries sampled in the two experiments. The energy loss studies have shown that the minimum in the $2^2B_g$ potential lies at least 1 eV lower in energy than the portion of the $2^2B_g$ surface accessed upon vertical electron attachment to the ground state of the neutral molecule.

CI calculations performed at the geometry of the $1^2A_u$ anion state (optimized at the UHF/3-21G level of theory) give a $1^2A_u \rightarrow 2^2B_g$ excitation energy about 0.5 eV lower than that found at the geometry of the neutral molecule while leaving the $1^2A_u \rightarrow 1^2B_g$ excitation energy relatively unchanged. This decrease is only 40% as large as that required to account for the difference in the excitation energies determined from the two experiments. It is possible that the calculations, due to the use of a relatively small basis set, underestimate the sensitivity of the excitation energy to the geometry. Preferential stabilization of the $2^2B_g$ state relative to the $1^2A_u$ state due to solvation could also account for part of the discrepancy.

It is of interest to compare the energies of the $1^2A_u \rightarrow 2^2B_g$ transition of the radical anion with those of the corresponding (i.e., paired) $1^2B_g \rightarrow 2^2A_u$ transition of the cation. Both gas-phase photodestruction measurements[21] and condensed-phase absorption measurements place the $1^2B_g \rightarrow 2^2A_u$ transition of the cation in the 4.2–4.4-eV range, in excellent agreement with the energy of the $1^2A_u \rightarrow 2^2B_g$ transition of the radical anion determined in the present study. However, this agreement may be fortuitous since

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(19) Spence, D. *J. Chem. Phys.* **1977**, *66*, 669.
(20) Doering, J. P.; McDiarmid, R. *J. Chem. Phys.* **1980**, *73*, 3617.
(21) Dunbar, R. C. *Chem. Phys. Lett.* **1980**, *32*, 508.

the results for the cation are at the geometry of the $1^2B_g$ state of the cation, while the energy spacings between the anion states determined from the energy loss and ETS measurements are at the geometry of the neutral molecule. It would be most constructive to compare the above results with the $1^2B_g \rightarrow 2^2A_u$ transition energy of the cation at the geometry of the neutral molecule. The necessary information could, in principle, be obtained from the photoelectron spectrum. Unfortunately, photoelectron spectroscopic studies do not yield a feature which can be unambiguously assigned to the $2^2A_u$ cation state.

## IV. Conclusions

The energy-loss spectra of butadiene provide evidence for $\pi^*$ anion states near 0.9 and 2.8 eV and $\pi^{-1}(\pi^*)^2$ anion states near 5.0, 6.7, 8.1, 11.0, and 12.5 eV. The two low-energy features are due to the $1^2A_u$ and $1^2B_g$ anion states, which have previously been assigned on the basis of ETS. The 5.0-, 6.7-, and 8.1-eV features are attributed to the $2^2B_g$, $2^2A_u$, and $3^2A_u$ anion states, respectively. The 5-eV anion state decays strongly into both the $1^3B_u$ and $1^1A_g$ states of the neutral molecule, indicating that it has both 1p and 2p-1h character, consistent with the predictions of CI calculations that both the $1a_u^2 1b_g 2a_u^2$ and $1a_u^2 1b_g^2 2b_g$ configurations make sizable contributions to the $2^2B_g$ anion state. The 11.0- and 12.5-eV features in the energy loss spectra are each attributed to one or more $\pi^{-1}(\pi^*)^2$ anion states.

There appear to be no assignments of the 1p-2h cation states of butadiene other than the lowest such state, which is paired with the 5-eV anion state studied here. We are also unaware of assignments of the higher lying anion states on the basis of absorption spectra of the radical anion in glasses. Indeed, the states observed in the energy loss spectrum at 6.7 and 8.1 eV would not be expected to be prominent in the absorption spectra, since transitions to these states from the ground-state anion are dipole-forbidden.

The 0.60- and 1.12-eV energy loss spectra both display a very broad feature centered near 8 eV, which is attributed to electron capture into one or more $\sigma^*$ orbitals. Finally, it is proposed that the series of weak, narrow features observed between 5.5 and 6.9 eV in the $1^3A_g$ and $1^1B_u$ excitation functions are due to $\pi^{-1}(3s)^2$ and $\pi^{-1}(3p)^2$ Feshbach resonances.

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**Registry No.** 1,3-Butadiene, 106-99-0.

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# Single-Crystal Molecular Structure Determinations and Theoretical Calculations on Alkynyl Sulfonate and Carboxylate Esters[†]

**Peter J. Stang,**[*,‡] **Charles M. Crittell,**[‡] **Atta M. Arif,**[‡] **Miriam Karni,**[§] **and Yitzhak Apeloig**[*,§]

*Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, and Department of Chemistry, Technion Israel Institute of Technology, Haifa 32000, Israel.*

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**Abstract:** The single-crystal X-ray structures of propynyl tosylate, **4**, and of ethynyl benzoate, **5**, were determined. Both esters are essentially linear acetylenes with $C\equiv C-O$ bond angles of 174.7° and 177.6°, respectively. The $C\equiv C-O$ acetylenic-oxygen bond length is 1.331 (4) Å in **4** and 1.329 (4) Å in **5**, significantly shorter than the analogous bond length in the corresponding saturated alkyl or vinyl esters. There is a concomitant increase in the S—O or $O-C(=O)$ bond lengths from saturated to vinyl (enol) to alkynyl esters. Ab initio molecular orbital calculations (6-31G*) for several smaller model systems are in excellent agreement with the X-ray geometries including the changes that occur as a function of R (R = alkynyl, vinyl, alkyl). $HC\equiv COSO_2R$, **7**, prefers a gauche conformation ($\angle HSCO = 70°$ for R = H and 76° for R = Me). The barriers to rotation around the S—O bond are 2.7 kcal mol$^{-1}$ in **7**, R = H, and 4.8 kcal mol$^{-1}$ in **7**, R = Me (6-31G*). The energies of several reactions of these esters have been calculated (MP3/6-31G*//6-31G*, kcal mol$^{-1}$). The calculated values below are given in the order $R = C\equiv CH \rightarrow R = CH=CH_2 \rightarrow R = CH_3$. Hydrolysis energies are -7.7, -4.1, and 3.5 for $HSO_2OR$ and -7.2, -2.9, and 3.0 for $ROC(=O)H$. The hydrogenation energies of the O—R bonds are -30.7, -17.3, and -21.8 in $ROSO_2H$, -30.3, -16.1, and -22.4 in $ROC(=O)H$, and -23.0, -13.3, and -25.4 in ROH. The hydrogenation energies of the RO— bond are -2.4, 1.1, and 8.8 in $RO-SO_2H$ and 2.8, 7.2, and 12.9 in $RO-C(=O)H$. Agreement with experimental data is good. The trends in the above energies as a function of R are discussed. The PM3 and AM1 calculations reproduce well the geometries of the alkynyl sulfonate and carboxylate esters but fail to reproduce these reaction energies.

## Introduction

Esters of all types play a key role in organic chemistry. They serve as valuable synthetic reagents, have important biological functions, and they have a place in mechanistic investigations. The three major classes of esters, carboxylates, sulfonates, and phosphates, are so ubiquitous that they are often taken for granted.

Recently, we reported the preparation of alkynyl sulfonates[1] **1**, carboxylates[2] **2**, and phosphates[3] **3**, members of the family of previously unknown, unique acetylenic esters that combine two

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[†] Dedicated to Professors Hiroshi Taniguchi and Yuho Tsuno on the occasion of their 60th birthdays.

[‡] University of Utah.

[§] Technion, Israel Institute of Technology.

(1) Stang, P. J.; Surber, B. W. *J. Am. Chem. Soc.* **1985**, *107*, 1452. Stang, P. J.; Surber, B. W.; Chen, Z. C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228.

(2) (a) Stang, P. J.; Boehshar, M.; Lin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7832. (b) Stang, P. J.; Boehshar, M.; Wingert, H.; Kitamura, T. *J. Am. Chem. Soc.* **1988**, *110*, 3272.

(3) Stang, P. J.; Kitamura, T.; Boehshar, M.; Wingert, H. *J. Am. Chem. Soc.* **1989**, *111*, 2225.