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ELECTROCHEMICAL AND PHOTOELECTRONIC SPECTRAL STUDY OF COMPOUNDS WITH HIGH IONIZATION POTENTIALS: ANODIC OXIDATION OF VINYL TRIFLATES IN APROTIC SOLVENTS

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Microelectrodes can be used to measure redox half-wave potentials in aprotic solvents containing no purposely added supporting electrolyte. By employing an electrode of sufficiently small size, the accessible potential range in solution is considerably extended. The electrochemical oxidation of vinyl (enol) triflates, which are oxidized at high electrode potentials, can therefore be studied using an ultramicroelectrode. Oxidation and ionization potentials, determined by ultramicroelectrode voltammetry and He I photoelectron spectroscopy, respectively, of 2-methylprop-1-enyl, cyclohexenyl, cyclopentenyl, 1,1-diphenylethenyl and prop-2-enyl triflate are reported. The results from electrochemical measurements and photoelectron spectra were compared.

INTRODUCTION

Since first introduced[1] over 20 years ago, a large variety of vinyl triflates have been prepared[2] and widely used in mechanistic, synthetic and organometallic chemistry. They serve as the prime precursors to both vinyl cations[3] and unsaturated carbenes,[4] and are involved in the formation of novel transition metal complexes.[5] More recently, enol triflates have been employed in olefin synthesis by coupling with organocopper reagents[6] and the directed formation of diverse conjugated dienes[7] by palladium-catalyzed coupling with organostannanes.[8] Vinyl triflates have also been utilized in the synthesis of unsaturated ketones,[9] aldehydes[9,10] esters[11] and amides[11] via carbonylative coupling reactions. Likewise, a variety of allyl alcohols may be formed by the $CrCl_2$–$NiCl_2$-mediated reaction of vinyl triflates with aldehydes.[12] Hence, vinyl triflates (enol triflates) have emerged as valuable reagents in organic chemistry.[13]

Despite the long history, ready availability[2,14–16] and increasing importance of vinyl triflates, little is known about their fundamental physico-chemical properties. We have therefore studied the electrochemical oxidation potentials and the photoelectron spectra of a series of representative vinyl triflates.

Electrochemical investigations of these systems have heretofore been precluded because their oxidation potentials are higher than those of conventional supporting electrolytes and most solvents. The use of electrodes of very small dimensions, or microelectrodes,[17] allows electrochemical experiments to be performed in polar solvents containing no purposely added electrolyte, and in non-polar solvents at high electrode potentials. In many cases, the elimination of the supporting electrolyte considerably extends the range of potentials that can be used. The observed half-wave potentials in this work were up to 1 V higher than those which can be observed in conventional electrochemical experiments. In addition, the measurements are made rapidly under steady-state conditions, so that interpretation of

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the data is simplified compared with that in conventional diffusion-controlled experiments. The oxidation potential determined from the electrochemical results were compared with ionization potentials determined from the gas-phase photoelectron spectra of several representative vinyl triflates.

EXPERIMENTAL

Reagents and chemicals. For electrochemical experiments, acetonitrile solvent (Burdick and Jackson, distilled in glass, 0·005% nominal water content) was distilled twice on a 150-cm glass helix packed column from calcium hydride and stored over drying alumina (Woelm Super Grade I) before use. The solvent was degassed immediately before use with dry helium (Matheson, research grade). 2-methylprop-1-enyl, cyclohexenyl, cyclopentenyl, 1,1-diphenylethyenyl and prop-2-enyl triflates were prepared by standard procedures.[2,14]

Photoelectron spectra. He I photoelectron spectra were obtained with a non-commercial instrument as described previously.[18] The spectra were calibrated against argon, and the resolution was less than 50 meV.

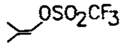
Electrochemistry. Microelectrodes were either purchased commercially (JAS Instrument Systems) or were prepared in the laboratory. Platinum ring microelectrodes were prepared by (a) coating the inner surface of capillaries with metal by vapor deposition or reduction of metal screen printing inks, followed by collapsing the capillary (over an oxygen–acetylene flame) around a glass fiber; and (b) using the same procedures to deposit platinum on a fine glass or quartz fiber, and collapsing a glass tube around it. The platinum ring electrode used in this work was 12 μm in diameter and had an average thickness of 500 Å. The secondary pseudo-reference electrode was a platinum wire placed about 0·5 mm from the tip of the working microelectrode. The cell consisted of a glass bulb designed to hold 15 ml of solution. The electrodes were mounted in the cell with ground joints. The cell was cleaned before use in hot acid solution (sulfuric acid–nitric acid, 1:1 v/v), rinsed in triply distilled water and dried in a vacuum at 110 °C. The cell assembly was mounted on steel clamps inside a 2 $\mathrm{ft}^3 \times 3/8$ in thick aluminum Faraday cage. Electrical connections were made though the cage by means of triaxial BNC-type bulkhead connectors. All cables used were triaxial, and were rigidly mounted to prevent triboelectric noise generation.

The electrode potential was maintained by a waveform generator (Hi Tek Instruments PPRl) added to a battery through a voltage adder. Currents were measured on a Keithley 617 picoammeter. The polarization curves were recorded on a Hewlett-Packard 7015 *x–y* recorder.

RESULTS AND DISCUSSION

Electrochemistry

The vinyl triflates **1–5** were chosen as simple prototypes of this class of compounds representing, primary, secondary, aryl and cyclic systems.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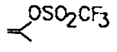
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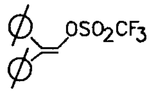
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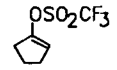
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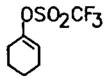
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Electrochemical oxidation of substituted vinyl triflates cannot be studied by conventional electrochemical techniques (such as cyclic voltammetry at macroelectrodes) owing to their typically high ionization potentials. The width of the potential window in a conventional electrochemical experiment is determined by the redox reactions of the solvent or supporting electrolyte. It is therefore impossible to study the redox reactions of species with very low electron affinities or high ionization potentials by ordinary electrochemical methods. In the aprotic solvent acetonitrile, which has one of the widest potential windows,[19] the accessible range is from about +3 V to about −3 V vs the $\mathrm{Ag/Ag^+}$ reference redox couple. It is now well known, however, that reducing the characteristic electrode dimensions to very small values allows measurements to be made in media of high resistivity.[17] Electrochemical experiments are therefore possible in solvents with little or no added supporting electrolyte, non-polar solvents, in solid solutions at low temperature and even in the gas phase. For example, studies have been performed on the oxidation of ferrocene in acetonitrile without purposely added supporting electrolyte, oxidation of chromium hexacarbonyl in pure dichloromethane, oxidation of aromatic hydrocarbons in pure benzene, oxidation of ferrocene in pure acetone down to −95 °C,[20] oxidations in low-temperature solid-solution eutectic mixtures and glasses of acetonitrile[21] and electrochemical oxidations and reductions in the gas phase.[22] These experiments are possible owing to the very small number of ions (and/or dipoles) required to charge the electrical double layer at the microelectrode.

Table 1. Ionization potentials (IP) and half-wave potentials ($E_{1/2}$) for the vinyl triflates

Triflate	Adiabatic IP (ev)	Vertical IP (eV)	$E_{1/2}$ (V)
2-Methylprop-1-enyl	9·05	9·52	3·32
Cyclohexenyl	9·10	9·48	3·33
Cyclopentenyl	9·17	9·55	3·34
1,1-Diphenylethenyl	8·19	8·62	3·62
Prop-2-enyl	9·76	10·31	3·63

In cases where the supporting electrolyte redox reactions limit the potential window, their elimination from solution allows the direct study of electron-transfer reactions of species with higher ionization potentials (or electron affinities) than the supporting electrolyte. An important example is the study of electrochemical oxidations in acetonitrile. The oxidation of the anion of all supporting electrolytes in this solvent will occur at potentials less than about 3 V vs Ag/Ag^+. We have recently demonstrated[19] that voltammetric data can be obtained at much higher oxidation potentials (up to ca 6 V vs Ag/Ag^+ under some circumstances), and have shown that it is possible to observe steady-state voltammetric behavior for compounds with vertical ionization potentials as high as 12·70 eV. These included n-heptane, cyclopropane, n-pentane, n-butane, methane and the rare gases.

The half-wave potentials (vs Ag/Ag^+) of the series of substituted vinyl triflates are listed in Table 1 and a typical polarization curve is shown in Figure 1. For comparison, it should be mentioned that the oxidation of ferrocene occurs at a half-wave potential of +0·95 V vs Ag/Ag^+ in acetonitrile solution containing no added supporting electrolyte,[20] and that the potential of the Ag/Ag^+ reference is 0·3 V more positive than that of the saturated calomel electrode in this solvent system.[23] The steady-state curves result from the fact that the mass transport coefficient to and from the microelectrode is very high. The plots were independent of all potential sweep rates used in these experiments (up to 10 V s^{-1}). Voltammetry was studied as a function of concentration of the substrate, and all limiting currents were linear with concentration over the range studied (0·01–10 mM in the vinyl triflate) to within 2% relative error. These observations indicate that the oxidations involving each of the vinyl triflates studied were electrochemically reversible at a microelectrode of sufficiently small size,[24] and the measured half-wave potentials are a good approximation to the expected standard oxidation potentials if the reference potential is taken into account. Standard potentials can only be measured under standard conditions (e.g. unit activities of both forms of the redox couple), but since it is impossible to know the activity coefficients of the species under study in this paper we regard the measured half-wave potential as the best possible estimate of the standard oxidation potential for a given vinyl triflate.

Photoelectron spectroscopy

The photoelectron spectra (PES) of 2-methylprop-1-enyl, prop-2-enyl, cyclopentenyl and cyclohexenyl triflates are shown in Figure 2. The spectra yield the adiabatic and vertical ionization potentials listed in

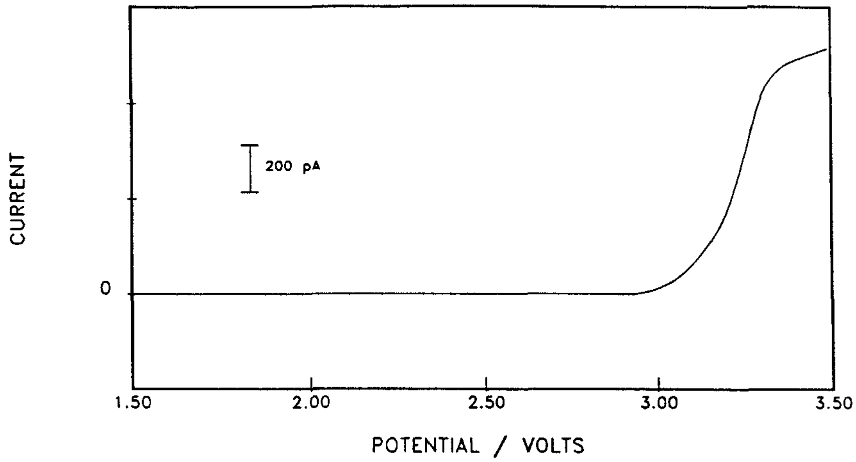


Figure 1. Polarization curve for the oxidation of **4** in pure acetonitrile at a platinum ring microelectrode. The sweep rate was 20 mV s^{-1}; potentials are vs Ag/Ag^+ (Electrode potentials were measured vs a Pt pseudo-reference and were rescaled to the Ag/Ag^+ reference; the potential of the Pt pseudo-reference was checked with ferrocene and 9, 10-diphenylanthracene internal standards). The curve on the reverse sweep superimposes the trace obtained on the forward potential excursion

Table 1. The broadness of the lowest ionization energy bands suggests an estimated error of ±0·05 eV in the measurements. It is interesting to note the high ionization energy for the prop-2-enyl triflate species (Figure 2A and Table 1) and the comparatively low ionization potential for the 1,1-diphenylethenyl species (Figure 2C and Table 1). The significant difference between the first ionization potentials of the prop-2-enyl and 2-methylprop-1-enyl triflates (Table 1) is surprising. The second and higher ionization potentials

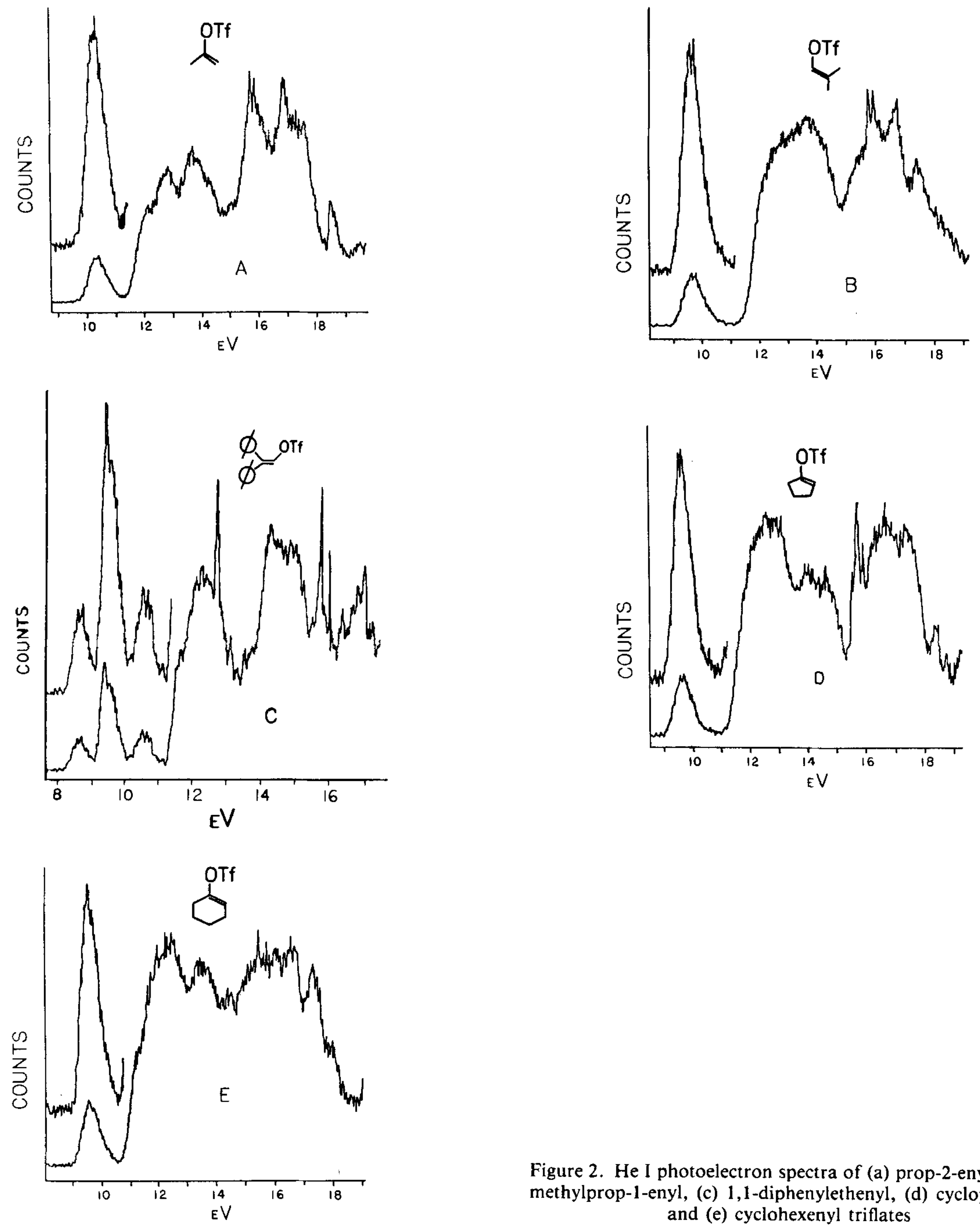


Figure 2. He I photoelectron spectra of (a) prop-2-enyl, (b) 2-methylprop-1-enyl, (c) 1,1-diphenylethenyl, (d) cyclopentenyl and (e) cyclohexenyl triflates

for these two species, however, are similar (Figure 2A and B). For the cyclopentenyl and cyclohexenyl systems the first ionization potentials are very similar, but higher ionization energies are more disparate (Figure 2C and D). The first ionization potentials (adiabatic and vertical, respectively) for the 1,1-diphenylethenyl triflate species are significantly lower than those of the remaining four triflates (Table 1 and Figure 2C). The band in the PES spectrum (Figure 2C) appearing at about 9·4 eV is similar to the lowest energy bands for the remaining four triflates (Table 1 and Figure 2A, B, D and E).

A plot of the vertical and adiabatic ionization potentials of the vinyl triflates is shown in Figure 3. As expected, there is certainly a correlation between the ionization potentials for the cyclohexenyl, cyclopentenyl, prop-2-enyl and the 2-methylprop-1-enyl triflates. The deviation from a 1:1 correlation for the half-wave potential and ionization potential for the diphenyl-substituted species may be explained by the difference in the solvation energy between the reduced and oxidized forms of this species. In the absence of secondary effects, such as large differences in the solvation energies of an oxidized and reduced form of a redox couple, a linear relationship between the oxidation potential and the vertical ionization potential of an electroactive species is to be expected. For a simple redox process:

$$\mathrm{O} + n\mathrm{e}^- = \mathrm{R}$$

the reversible potential is given by the expression[19]

$$E^0_{\text{rev}} = \frac{1}{nF}\left[\Delta G^0_{\text{R}}(\text{solvation}) - \Delta G^0_{\text{O}}(\text{solvation})\right] + \frac{I_{\text{p}}}{nF} - E^0_{\text{ref}}$$

where the term in brackets represents the change in free energy of solvation between the reduced and oxidized forms of the couple, n is the number of electrons exchanged per mole of reactant, F is the Faraday constant, I_{p} is the ionization potential and E^0_{ref} is the standard potential of the reference electrode. The same type of relationship will exist in non-standard states if the activities of the species are taken into account:

$$E_{\text{rev}} = E^0_{\text{rev}} + \frac{RT}{nF}\ln\left(\frac{a_{\text{O}}}{a_{\text{R}}}\right)$$

where a_{O} and a_{R} are the activities of the oxidized and reduced forms at the electrode surface, respectively. We then see that if the difference between the solvation energies of the reduced and oxidized forms is large, then the half-wave potential for the reaction will be lower than when the standard free energies of the two species are equal. For ions that are effectively solvated, the linear relationship is generally obeyed fairly well. Solvation of ionic species can only occur after there is solvent structure rearrangement or breaking; this is an endothermic process which ultimately reduces the total effect of the magnitude of the difference in the standard free energy of solvation of the species. It is well known, however, that smaller ions typically show a considerable departure from linear behavior of $E_{1/2}$ and I_{p} with unit slope; very small ions having a high charge density are expected to be more efficiently solvated into the solvent cage structure. The difference in the solvation energies of the neutral and oxidized species is therefore large, and a large change in the magnitude of the half-wave potential is observed; the shift is always to more negative potentials for oxidations. Expected oxidation potentials for the vinyl triflates under study, based on observed ionization energies (Figure 2), would be much lower than actually observed.[25] Hence the solvation energies of all of the vinyl triflates under study here are appreciable.

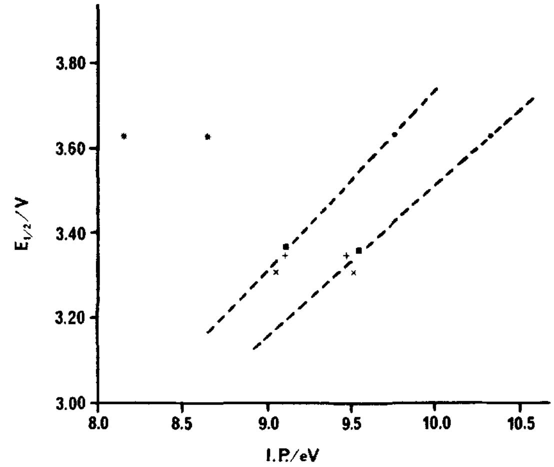


Figure 3. Plot of the electrochemical half-wave potentials (vs. Ag/Ag$^+$) as a function of the adiabatic and vertical ionization potentials for the substituted triflates. For each triflate the lower value for the ionization potential is the adiabatic value. ×: 2-methylprop-1-enyl; +: cylcohexenyl; ■: cyclopentenyl; *: 1,1-diphenylethenyl; •: prop-2-enyl

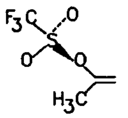
The linear correlation between oxidation potential and ionization energy is obeyed fairly well for all of the vinyl triflates studied except the diphenyl-substituted species (Figure 3). This suggests that the solvation energy for the diphenylvinyl species is considerable; a similar result has been observed previously in strained aromatic cycloproparene systems.[26] Another possibility for the disparity involving the diphenyl-substituted triflate is that the conformation of this molecule in solution may be substantially different from its conformation in the gas phase. It is difficult to explain the high oxidation potential measured for 1,1-diphenylethenyl triflate in the light of its low first ionization potential obtained in the gas phase.

However, in solution, as a result of solvation, the overall valence orbital electron density of this species may more closely resemble that of the other vinyl triflates studied. The implication is that the feature appearing in the gas-phase photoelectron spectrum at 9·4 eV (Figure 2C) is a more realistic estimate of the actual ionization potential of the molecule in solution. If this is the case, then the measured half-wave potential of the diphenyl-substituted species (Table 1) is actually within the expected range in the light of the PES results obtained for the other vinyl triflates.

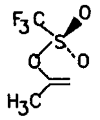
The molecular energy minimization program Macromodel 2 (MM2)[27] was used to carry out geometry optimizations on the vinyl triflates. Molecular orbital energies were then calculated using AM1 software[28] within the Macromodel package; AM1 estimations are generally more accurate than MNDO and MNDO/3 methods.[28]

Two conformations were used as starting points for the MM2 optimizations. One initial geometry had the sulfur atoms *cis* to the carbon—carbon double bond and the other held the sulfur *trans* to the vinyl group. For the moelcular orbital calculations typical bond lengths, bond angles and force constants were input initially, and the molecular orbital eigenvalues (MOES) for the energy-minimized geometries were obtained iteratively in the calculation. From these energy minimizations MOES for the highest occupied molecules orbitals (HOMOS) were estimated and compared with observed vertical ionization potentials.

Table 2 compares the optimized MOES for the vinyl triflates with experimentally determined vertical ionization energies. It is seen that the configuration, *cis* or *trans*, has little influence on the stabilization energy of the HOMO for the cyclopentenyl and cyclohexenyl triflates. However, for prop-2-enyl triflate the *trans* configuration yields a significantly more stabilized MOE than does the *cis* geometry. Here the dihedral angle between the two double-bonded carbons, the oxygen bridging one of these sp^2 carbons to the sulfur and the sulfur atom is approximately 109° (Table 2). Hence the sulfur is above the plane of the π-system of the ene carbons, and the molecule is twisted:



In the case where the sulfur is *cis* to the double bond (for the prop-2-enyl species) the dehidral angle between the two ene carbons, the bridging oxygen and the sulfur is only about 3° (Table 2). Hence this molecule is more or less planar since the sulfur is approximately in the same plane as the oxygen and the vinyl carbons:



For the two ring systems studied, there is little difference in the HOMO energy whether the sulfur is *cis* or *trans* to the C=C double bond. In these cases the sp^2 carbon—sp^2 carbon—bridging oxygen—sulfur dihedral angle is close to zero in all cases, whether the sulfur atom is *cis* or *trans* to the vinyl group. Hence planarity is favored in these systems regardless of the configuration of the sulfur atoms (Table 2). The sulfur is above the plane (twisted) with respect to the plane of the π-system only in the case of *trans*-prop-2-enyl triflate.

The molecular orbital computations indicate that the HOMO is π-type for each of the near-planar systems, with the exception of the 1,1-diphenylethenyl species, which shows five low-lying MO eigenvalues; this is in accord with the photoelectron spectrum (Figure 2C). The HOMO is π-type benzene, as one would expect. It is the fifth highest band at 10·4 eV which is similar to the HOMOs of the other triflates. In the case of *cis*-prop-2-enyl triflate, the HOMO (MOE = 10·22 eV) involves π-bonding p-orbitals of the C=C double bond, the bridging oxygen and the methyl group. This is also the case for the HOMOS of 2-methylprop-1-enyl, cyclopentenyl (*cis* and *trans*) and cyclohexenyl (*cis*

Table 2. Molecular orbital eigenvalues (MOEs), vertical ionization energies and C=C—O—S dihedral angles for the vinyl triflates

Triflate	Configuration	MOE (ev)	IP_v (eV)	C=C—O—S dihedral angle (°)
Prop-2-enyl	*trans*	10·56	10·31	109·1
	cis	10·22		3·4
2-Methylprop-1-enyl	*trans*	9·84	9·52	3·9
Cyclopentenyl	*trans*	9·77	9·55	6·9
	cis	9·78		4·5
Cyclohexenyl	*trans*	9·72	9·48	2·1
	cis	9·75		5·9
Diphenylethenyl	*trans*	8·50	8·62	4·5

and *trans*) triflates. The result is that the MOE for the HOMO and hence the magnitude of the lowest ionization energy depend on the degree of interaction between the oxygen and the C=C double bond. Hence the vertical ionization potential depends on the dihedral angle between the atoms in the C—C—O—S portion of the triflate molecule. In the case of twisted *trans*-prop-2-enyl triflate, where the MOE (and IE) is lower in energy, the HOMO is different; it has contributions from the SO_2 fragment and is stabilized with respect to the planar *cis*-prop-2-enyl species (Table 2).

For higher ionization potentials MOE assignments such as those made above are less reliable. This is because the triflate systems studied here consist of many atoms and are largely asymmetric. Only higher energy MOES for asymmetric molecules with very few atoms (usually five or less) can be satisfactorily approximated by modeling methods.

In the case of 2-methylprop-1-enyl triflate, a nearly planar configuration is the stablest structure. In this molecule a twisted conformation yields destabilized MOEs for the HOMO. For cyclopentenyl and cyclohexenyl triflates nearly planar conformations are the stablest structures regardless of whether the sulfur is *cis* or *trans* to the ene moiety. A planar configuration is also favored for the 1,1-diphenylethenyl species in the gas phase, but the high oxidation potential of this molecule suggests that its conformation in solution may be different from its geometry in the gaseous state. The fact that the MOEs are higher than the IEs (Table 2) for 2-methylprop-1-enyl, cyclopentenyl and cyclohexenyl triflate (and this is generally observed in most systems) provides support that in the case of prop-2-enyl triflate the twisted conformation is favored in the gas phase.

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