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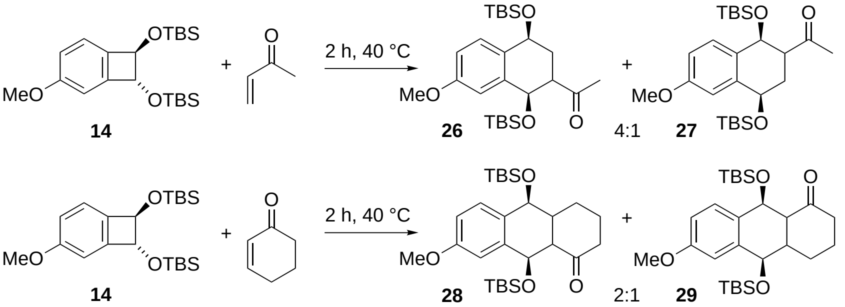
[12] The Diels–Alder reaction of **14** with methyl vinyl ketone gave a 4:1 ratio of regioisomers **26**:**27**, while that between 2-cyclohexen-1-one and **14** gave a 2:1 ratio of **28**:**29**. Poor regioselectivity of 4-methoxy-substituted *o*-quinone dimethides in Diels–Alder cycloadditions is precedented in reactions with methyl acrylate: Y. Ito, M. Nakatsuka, T. Saegusa, *J. Am. Chem. Soc.* **1982**, *104*, 7609. For information regarding the regiochemistry of **13**, see reference [3].



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First Experimental Observation on Different Ionic States of both Methylthio ($CH_3S^{\bullet}$) and Methoxy ($CH_3O^{\bullet}$) Radicals[**]

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When combined with ab initio or density-functional theory (DFT) calculations, HeI photoelectron spectroscopy (PES) richly provides information on orbital energies, ionic states, bonding, and vibrational fine structure data that cannot be easily obtained by other experimental techniques. While there have been many PE spectroscopic studies of stable closed-shell molecules over the past 30 years, corresponding studies of open-shell radicals have been fewer.[1–3] Both the methylthio ($CH_3S^{\bullet}$)[4–14] and methoxy ($CH_3O^{\bullet}$)[15–18] radicals are important intermediates in combustion, photochemical smog and atmospheric reactions. The competitive effects of the dynamic Jahn–Teller distortion and spin–orbit coupling and their influences on the ground states of both $CH_3S^{\bullet}$ and $CH_3O^{\bullet}$ are the subject of numerous experimental and theoretical studies.[19–26]

Studies on these two radicals have been based on ab initio calculations to determine the energetics and geometry of the $CH_3S^{\bullet}$ radical in its ground and excited electronic states,[27–29] but as yet there is no report on the different ionic states for $CH_3S^{\bullet}$ or of direct experimental evidence of the ionization energies of different ionic states for $CH_3O^{\bullet}$. Two separate photoionization mass spectrometry (PIMS) studies gave the first ionization energy of the $CD_3O^{\bullet}$ isotopomer ((10.726 ± 0.008) eV,[23] (10.74 ± 0.02) eV[30]). Slightly different calculated ionization energies of $CH_3O^{\bullet}$ have been reported by Curtiss et al.[20] and Dyke et al.[25] (10.78 and (10.72 ± 0.02) eV, respectively). Clearly, experimental measurements of the ionization energies for both radicals are necessary.

In our laboratory, we generate a well characterized source of radicals or atoms by in situ pyrolysis and microwave discharge of precursor molecules.[31–35] In this communication, we would like to report the PES studies on the electronic structures of both methylthio and methoxy radicals. To our knowledge, this is the first experimental observation of different ionic states for both radicals.

The methylthio radical

The thermal, homolytic dissociation of suitable precursors is the most widely used method for generating radicals. Thermal decomposition of disulfides gives alkylthio radicals.[36] Calculations on CH_3SSCH_3 indicate that the S–S bond is the weakest present and therefore pyrolysis of CH_3SSCH_3 offers a simple route to the $CH_3S^{\bullet}$ radical [Eq. (1)].

$$CH_3SSCH_3 \xrightarrow{(285\pm0.5)\,°C} 2\,CH_3S^{\bullet} \tag{1}$$

Figure 1a shows the in situ PE spectrum of the species generated by pyrolysis of the CH_3SSCH_3 molecule at 285 °C and Figure 1b shows the lower ionization energy region ($E <$ 11.00 eV) in greater detail. The three bands at $E = 9.26$, 9.91, and 10.32 eV are very sharp and correspond to the ionization of nonbonding electrons of the generated radical, because, in this case, the vertical ionization energy E_V is equivalent to the adiabatic ionization energy E_A. The first ionization energy of the $CH_3S^{\bullet}$ radical[36] (9.26 eV) is in good agreement with both

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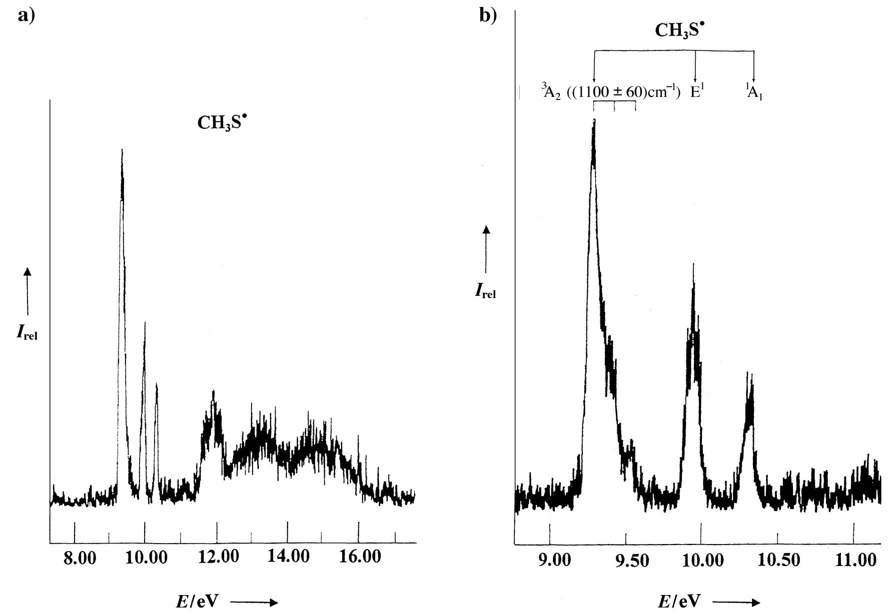

Figure 1. a) An in situ HeI-PE spectrum (given as relative intensities I_{rel}) of the product ($CH_3S^•$) from the pyrolysis of CH_3SSCH_3; b) the expanded spectrum in the lower ionization energy region ($E < 11.00$ eV).

adiabatic ionization energy values obtained from two PIMS studies[37, 38] and a G2 first ionization energy calculation (9.25 eV).[39, 40] The vibrational fine structure spacing of this band also supports the assignment, as the spacing energy ($\tilde{\nu} = (1100 \pm 60)\mathrm{cm}^{-1}$) is in good agreement with the presence of the ν_{C-S} stretching mode of the CH_3S^+ ion ($\tilde{\nu} = (1098 \pm 2)\mathrm{cm}^{-1}$).[14, 41]

Assignment of the sharp bands (Figure 1) to ionic states proceeds as follows: According to the C_{3v} symmetry of $CH_3S^•$, as determined by a microwave study,[8] and assuming a $\tilde{\chi}^2E$ ground state, as proposed by theoretical studies,[39, 40], the valence shell molecular orbitals would be, in the order of increasing energy, $(5a_1)^2(2e)^4(6a_1)^2(7a_1)^2(3e)^3$. The HOMO (3e) is essentially derived from the nonbonding lone-pair orbital of the sulfur atom with a smaller contribution from C–S antibonding. The removal of an electron from the HOMO will generate a CH_3S^+ ion in the $^3A_2$, ^1E, and $^1A_1$ ionic states ($J = 1,½,0$, respectively) and the three PES bands corresponding to these three ionic states of $CH_3S^•$ should be very sharp. The degeneracy of the ionized states is given by $2J + 1$, so that the ratio of the PES band areas of the ionic states should be 3:2:1 for $^3A_2$:^1E:$^1A_1$. Figure 1b reveals an band area ratio of 3.02:1.95:1.00 for the bands at $E = 9.26$, 9.91, and 10.32 eV, respectively, which is very close to the expected ratio. The measured PE spectrum has provided, for the first time, evidence of different ionic states of the $CH_3S^•$ radical.

This assignment of the PES bands for $CH_3S^•$ is also supported by the results of improved DFT calculations on the ground state of the $CH_3S^•$ radical and of the ground and (several) ionic states of the CH_3S^+ ion. Such a calculation was used to assign PES bands for a number of other radicals.[32, 34, 35] Table 1 includes the ionization energies E, as determined by the maxima of the bands in the PE spectra, and the computed ionization energies E_v for different ionic states of $CH_3S^•$. According to the Frank–Condon principle, E_V is obtained from the total energy difference between the ground states of the cation and the neutral radical in C_{3v} symmetry. According to Table 1 the low energy ionization energies from the PE spectrum for the $CH_3S^•$ radical (9.26, 9.91, and 10.32 eV) are in good agreement with the computed ionization energies (9.266, 10.024, and 10.421 eV).

The higher energy PES bands for the methylthio radical at $E = 11.92$, 13.60, and 14.73 eV (Figure 1 a) are very broad, which indicates that the corresponding ionized electrons occupied bonding orbitals or several orbitals of $CH_3S^•$. The broad PES band at 11.92 eV is assigned to the ionization of the $7a_1$ orbital to consquently form both triplet ^3E and singlet ^1E ionic states. This assignment is supported on the basis of the computed ionization energies of 11.724 (^3E) and 12.156 eV (^1E) as the two states are very similar in energy and thereby appear overlapped. Similarly, the broad PES band at 13.60 eV is assigned to the ionization of the $6a_1$ orbital as the computed ionization energies of the formed triplet and singlet states 12.810 (^3E) and 13.916 eV (^1E) are again close and overlap. The very broad band at 14.73 eV is assigned to ionization of the less energetic valence orbitals of $CH_3S^•$.

Table 1. PES ionization energies E, computed (DFT) ionization energies E_V, and relative intensities I_{rel} of signals observed from different ionic states for the methylthio radical.

E(PES) [eV][a]	E_V(DFT) [eV]	Cationic state	Relative intensity measured[b]	Relative intensity expected
9.26	9.266	$^3A_2$	3.02	3
9.91	10.024	^1E	1.95	2
10.32	10.421	$^1A_1$	1.00	1
11.92	11.724	^3E		
	12.156	^1E		
13.60	12.810	^3E		
	13.916	^1E		
14.73	15.102	$^3A_2$		

[a] Values are ±0.02 eV and derived from the maxima of the PES bands. [b] Corrected for analyzer sensitivity ±0.02.

The methoxy radical

The incomplete combustion of methanol leads to the production of the methoxy radical, which, in the presence of nitrogen oxides, produces the mutagenic methyl nitrite $CH_3ONO^•$.[42] Methyl nitrite has also attracted considerable attention from atmospheric contamination studies since photodissociation processes cleave the molecule into NO and $CH_3O^•$ species.[43–46] That is, methyl nitrite can be used as a source of methoxy radicals. We generate a $CH_3O^{\bullet}$ source by pyrolysis of CH_3ONO at 275 °C and its PE spectrum was recorded in situ.

The dissociation of CH_3ONO to produce $CH_3O^{\bullet}$ and NO, should lead to contamination of the PE spectrum of $CH_3O^{\bullet}$ with bands due to the NO species. Figure 2a shows the PE spectrum of products generated by pyrolysis of CH_3ONO and Figure 2b shows the lower ionization energy region ($E <$ 14.00 eV) in greater detail. Five bands in the region $E <$ 10.70 eV can be assigned to NO since the fine structure energy ($\tilde{\nu} = 2260\,cm^{-1}$) and the band at 9.54 eV with the greatest local intensity match the bands of NO alone. The two bands in the higher energy region ($E = 16.56$ and 18.32 eV) are also characteristic of NO species. The remaining bands in Figure 2 are therefore derived from the ionization of $CH_3O^{\bullet}$.

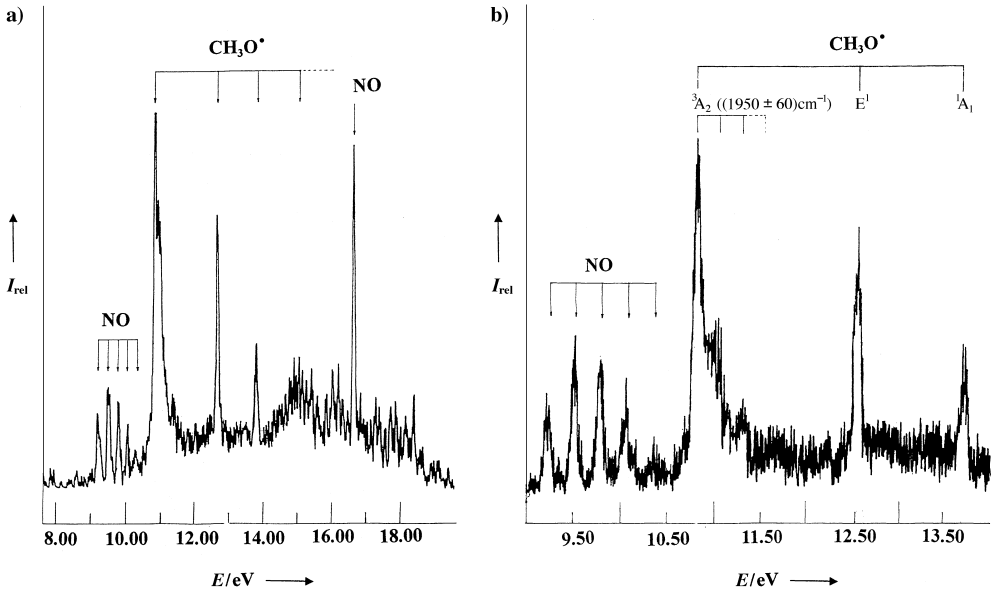

Figure 2. a) An in situ HeI-PE spectrum (given as relative intensities I_{rel}) of the products ($CH_3O^{\bullet}$ and NO) from the pyrolysis of CH_3ONO; b) the expanded spectrum in the lower ionization energy region ($E < 14.00$ eV).

Assignment of the three sharp bands in Figure 2 for $CH_3O^{\bullet}$ follows the same process used for $CH_3S^{\bullet}$: For C_{3v} symmetry and a ^2E ground state, the molecular orbitals would be, in the order of increasing energy, $(3a_1)^2(4a_1)^2(1e)^4(5a_1)^2(2e)^3$. The HOMO (2e) of $CH_3O^{\bullet}$ has a dominant contribution from the lone-pair electrons of the oxygen atom with a small degree of C–O antibonding character.[20]. The removal of an electron from the HOMO will generate a CH_3O^+ ion in the $^3A_2$, ^1E, and $^1A_1$ states. The sharp band at 10.78 eV matches the computed G2 adiabatic ionization energy (10.78 eV[20]), and is in good agreement with the reported first ionization energy of the $CD_3O^{\bullet}$ isotopomer from two PIMS studies ((10.726 ± 0.008)[23] and (10.74 ± 0.02) eV[30]). This band is therefore attributed to the A_2 ionic state of CH_3O^+ and the vibrational fine structure spacing ($\tilde{\nu}(1950 \pm 60)\,cm^{-1}$) is as expected for a ν_{C-O} stretching mode. The bands at 12.50 and 13.72 eV are designated as the ^1E and $^1A_1$ ionic states of CH_3O^+, respectively, because of the sharpness of the bands and because the expected 3:2:1 band area ratio for $^3A_2$:^1E:$^1A_1$ is indeed observed (3.11:2.01:1.00 for the bands at 10.78, 12.50, and 13.72 eV).

This assignment is again supported by the improved DFT calculations performed in a manner similar to those for the methylthio radical. The calculation presumed a $\tilde{\chi}^2E$ ground state and the radical and its ionic states were restricted to C_{3v} symmetry. The total energy of the singlet state, described by a multideterminant wave function, was calculated using the the sum method of Ziegler et al.[47] Table 2 shows the good agreement between the ionization energies measured ($E = 10.78\,(^3A_2)$, $12.50\,(^1E)$, and $13.72\,(^1A_1)$ eV) and calculated ($E = 10.791$, 12.502, and 13.728 eV). Also of interest is a vibrational fine structure at $\tilde{\nu} = (1950 \pm 60)\,cm^{-1}$ present on the first band but absent on the other two. This phenomenon is currently under investigation.

Finally, the broad, higher energy PES band at 15.20 eV (Figure 2a) can be assigned to ionization of electrons of the $5a_1$ orbital leading to the ^3E and ^1E ionic states (calculated ionization energies are 14.994 (^3E) and 15.381 eV (^1E)).

Table 2. PES ionization energies E, computed (DFT) ionization energies E_V, and relative intensities I_{rel} of signals observed from different ionic states for the methoxy radical.

E(PES) [eV][a]	E_V(DFT) [eV]	Cationic state	Relative intensity measured[b]	Relative intensity expected
10.78	10.791	$^3A_2$	3.11	3
12.50	12.502	^1E	2.01	2
13.72	13.728	$^1A_1$	1.00	1
15.20	14.994	^3E		
	15.381	^1E		

[a] Values are ±0.02 eV and derived from the maxima of the PES bands. [b] Corrected for analyzer sensitivity ±0.02.

In summary, the PE spectra of both $CH_3S^{\bullet}$ and $CH_3O^{\bullet}$ radicals provide direct experimental evidence for the existence of different ionic states. The C_{3v} symmetry of both radicals could be deduced from their respective PE spectra. The PE spectrum is therefore able to provide both the orbital energy levels and also molecular symmetry.

Experimental Section

Experiments were performed on a double-chamber ultraviolet-photoelectron spectrometer (UPS), which was built specifically to detect transient species.[48] The continuous $CH_3S^{\bullet}$ or $CH_3O^{\bullet}$ radical beams were produced in situ by pyrolysis of gas-phase CH_3SSCH_3 at (285 ± 0.5) °C or CH_3ONO at (275 ± 0.5) °C, respectively, in a quartz tube. The heating system employed a double-heater inlet device. The purity of CH_3SSCH_3 was compared to a reference PE spectrum.[49]. The CH_3ONO was prepared by standard methods[50, 51] and its purity was comfirmed by mass spectrometry and by a reference PE spectrum[46]. The UPS delivered an operational resolution of about 30 meV for the $^2P_{3/2}$ band of Ar$^+$. Experimental ionization energies were calibrated by the simultaneous addition of small amounts of Ar and CH$_3$I with the sample.

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The Kinetic Order of an Interfacial Diels–Alder Reaction Depends on the Environment of the Immobilized Dienophile[**]

Muhammad N. Yousaf, Eugene W. L. Chan, and Milan Mrksich[*]

Substituent effects are used widely in physical organic chemistry to elucidate the relationships between the structures, reactivities, and properties of molecules. This mechanistic tool finds routine use in many areas, including the determination of reaction mechanisms,[1] the development of catalysts,[2] and the design of selective inhibitors of proteins.[3] We have a program to extend the principles of physical organic chemistry to the reactions of molecules confined at the solid–liquid interface in order to elucidate the factors that uniquely affect these reactions. Here we show one such effect wherein the reaction of an immobilized molecule is influenced by a substituent effect arising from the surrounding microenvironment. We use the Diels–Alder reaction of soluble cyclopentadiene with quinone immobilized to a self-assembled monolayer (SAM) on gold as a model system.

This work uses monolayers prepared from an alkanethiol terminated in a hydroquinone group and a second alkanethiol terminated in either a methyl or hydroxy group (Figure 1). The reversible two-electron electrochemical oxidation of this hydroquinone to the quinone is well known.[4] In previous work we showed that this quinone undergoes a Diels–Alder reaction with cyclopentadiene (Cp) dissolved in the electrolyte to give the cycloaddition adduct.[5] Since this adduct is not

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