COMMUNICATION

Thermolysis of 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline studied with photoelectron spectroscopy. He(I) photoelectron spectrum of dimethoxycarbene

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Abstract: Gas phase thermolysis of 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (**1**) in an ultraviolet photoelectron spectrometer by means of a CW CO_2 laser as directed heat source at 26 W gave a complex PE spectrum that included ionization bands belonging to acetone, tetramethoxyethylene (**3**), and dimethyl oxalate (**4**). Subtraction of the spectra of acetone, **3**, and **4** from the pyrolysis spectrum of **1** left a simple PE spectrum that is attributed to dimethoxycarbene (**2**) along with some ethane. Becke3LYP/6-31+G* calculations gave first adiabatic and vertical ionization potentials of **2** as well as orbital energies that are in perfect agreement with experimental values. From the available experimental and calculational data, **2** is assumed to adopt a *w* conformation.

Key words: dimethoxycarbene, 2,2-dimethoxy-Δ^3-1,3,4-oxadiazoline, tetramethoxyethylene, He(I) photoelectron spectroscopy, thermolysis.

Résumé : La thermolyse en phase gazeuse de la 2,2-diméthoxy-5,5-diméthyl-Δ^3-1,3,4-oxadiazoline (**1**) dans un spectromètre photoélectronique ultraviolet, à l'aide d'un laser à CO_2 CW utilisé comme source dirigée de chaleur à 26 W, conduit à un spectre PE complexe comportant des bandes d'ionisation appartenant à l'acétone, au tétraméthoxyéthylène (**3**) et à l'oxalate de diméthyle (**4**). Si l'on soustrait les spectres de l'acétone et ceux des composés **3** et **4** du spectre de pyrolyse du composé **1**, on obtient un spectre PE résiduel qui a été attribué au diméthoxycarbène (**2**) en présence de faibles quantités d'éthane. Des calculs de Becke3LYP/6-31+G* ont permis d'obtenir les premiers potentiels d'ionisation adiabatique et verticale de l'entité **2** ainsi que des énergies d'orbitales qui sont en parfait accord avec les valeurs expérimentales. Sur la base des données expérimentales et résultats des calculs, on peut faire l'hypothèse que l'entité **2** adopte une conformation *w*.

Mots clés : diméthoxycarbène, 2,2-diméthoxy-Δ^3-1,3,4-oxadiazoline, tétraméthoxyéthylène, spectroscopie photoélectronique He(I), thermolyse.

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The combination of photoelectron (PE) spectroscopy with quantum chemical calculations of molecular orbital eigenvalues and eigenvectors gives information about the electronic structure and bonding of stable as well as transient species that is provided by no other technique. PE spectra of transient carbenes are very rare (1) due to the high reactivity of these species, which requires special instrumentation. Usually, reactive intermediates are generated pyrolytically from thermally labile

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precursors using electrically heated furnaces that are several centimeters in length (2). Yet carbenes have to be generated close to the ionization beam to minimize the incursion of reactions like rearrangement, fragmentation, or dimerization. Our unique ultraviolet PE spectrometer – CW CO_2 laser apparatus (3) allows us to use the laser as a directed heat source to produce a hot zone as short as 1 mm in length on the tip of a quartz tube positioned at about 1 cm from the point of intersection with the ionization beam. We used this setup successfully to obtain PE spectra of short-lived reactive species such as benzazete and *o*-benzyne (4), 1,2-cyclohexadiene (5), 1-(2-thiaindane)ketene and benzocyclobutenethione (6), as well as *p*-substituted phenylketenes (7) through pyrolyses of suitable precursors (Scheme 1).
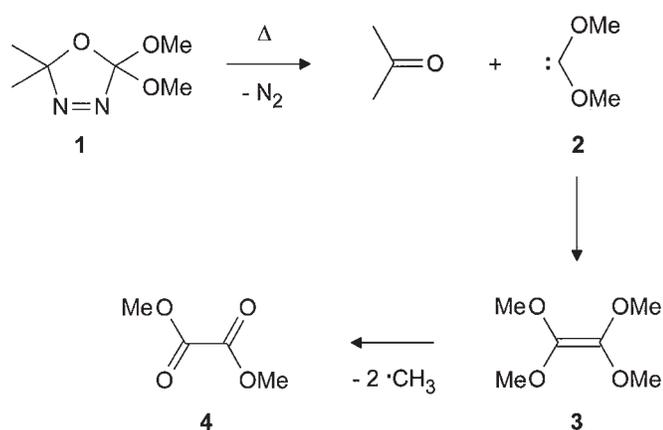
We decided to study the thermal gas phase decomposition of 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (**1**) (8), because thermolysis in solution had shown formation of

Scheme 1.

Fig. 1. He(I) photoelectron spectra of
(*a*) 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (**1**); (*b*) the
pyrolysate of **1** obtained at a laser power level of 26 W; (*c*)
tetramethoxyethylene (**3**); (*d*) dimethoxycarbene (**2**) after
subtraction (the hatched bands are due to ethane). Uniformly
shifted calculated eigenvalues (Becke3LYP/6-31+G*) are given as
vertical bars in (*a*) and (*d*).
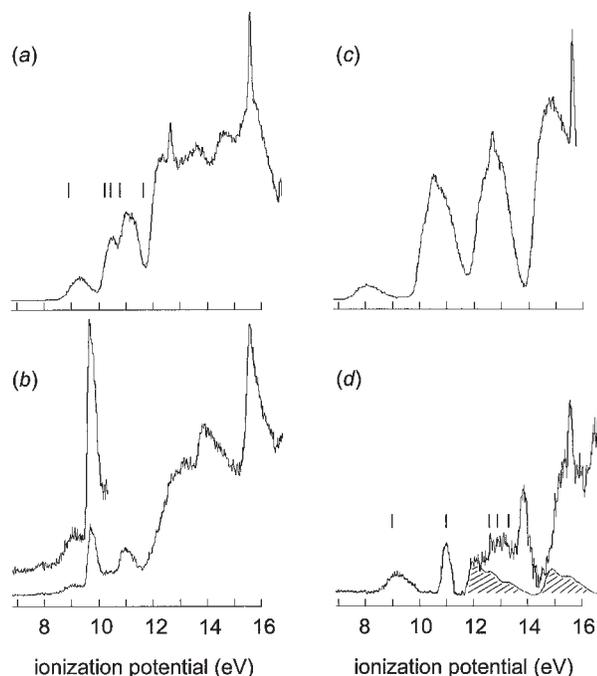
tetramethoxyethylene (**3**) (9) and preliminary flash vacuum
pyrolysis experiments on **1** gave dimethyl oxalate (**4**), both of
which could arise from a common precursor, dimethoxycar-
bene (**2**). Our recent computational study on the first adiabatic
and vertical ionization potentials of carbenes (10) provided us
with a calculational method (Becke3LYP/6-31+G* (11)) for
the reliable prediction of these values. Applying these calcu-
lations to dimethoxycarbene (**2**), we expected to identify **2**
through its ionization potentials if its spectrum actually was
present in the pyrolysis spectrum of **1**, and possibly to establish
its conformation. The particular choice of oxadiazoline **1** for
this study was made because (*a*) it is a source of **2**; (*b*) it gave

Fig. 2. Preferred conformation (Becke3LYP/6-31+G*) of (*a*)
oxadiazoline **1** and (*b*) conformers **2w** and **2sk** of dimethoxycarbene.
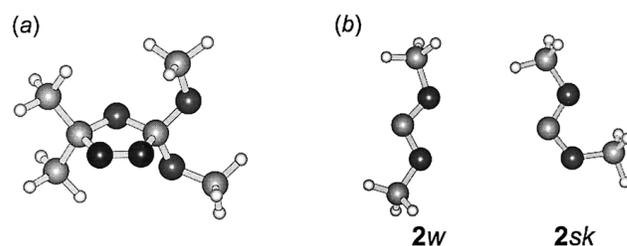
Table 1. Total energies E_T (hartrees) and calculated ionization
potentials IP (eV) of optimized geometries of **1**–**3** (N electrons) and
their radical cations (N–1 electrons) according to Becke3LYP/6-31+G*.

	Number of electrons	E_T	IP
1	N	–571.004 434	
	N–1 [a]	–570.677 705	8.89
2w	N	–268.309 870 [b]	
	N–1 [c]	–268.011 517	8.29
	N–1 [a]	–267.978 827	9.01
2sk	N	–268.306 911 [d]	
	N–1 [c]	–268.008 806	8.11
	N–1 [a]	–267.975 877	9.01
3	N	–536.693 043 [e]	
	N–1 [c]	–536.445 198	6.68
	N–1 [a]	–536.403 737	7.87

[a] Single-point energy calculation on the molecule's optimized geometry
for IP_v.
[b] E_T corrected for zero-point vibrational energy is –268.220 668.
[c] The geometry of the radical cation was optimized for IP_a.
[d] E_T corrected for zero-point vibrational energy is –268.217 754.
[e] For the all-*anti* conformer.

us the additional opportunity to compare the mode of its de-
composition (on a different path **1** can also yield nitrogen,
dimethylcarbene, and dimethyl carbonate) in the gas phase to
that in solution (9); and (*c*) it is the first member in a series of
similar oxadiazolines that could be used as possible precursors
of O,S- and O,N-substituted carbenes in the gas phase. In this
communication, we report the results of a He(I) PE spectro-
scopic study of the thermolysis of oxadiazoline **1** along with
ab initio (Gaussian 94 (12)) calculational data on **1** and two of
its pyrolysis products, dimethoxycarbene (**2**) and tetra-
methoxyethylene (**3**). PE spectra for **2** and **3** are presented for
the first time.

The PE spectrum of **1** is shown in Fig. 1*a*. Three bands
belonging to four ionizations (at 9.30, 10.49, 11.00, and 11.22
eV) are separated from the main group of bands with its first
band at about 12.1 eV. The sharp peak at 12.63 eV belongs to
traces of water. Vertical bars in Fig. 1*a* give negative
Becke3LYP/6-31+G* orbital energies (–ε 6.81, 8.11, 8.33,
8.74, and 9.49 eV), which are shifted so that the HOMO energy
equals that of the calculated first vertical ionization potential
IP_v (8.89 eV; total energies are given in Table 1). Support for
applying a Koopmans' Theorem-like interpretation of orbital
energies at the DFT level of theory in PE spectroscopic studies
has been provided by Arduengo et al. (1*d*). The most stable
conformation of **1**, with methoxy groups "sickle" as shown in
Fig. 2*a*, was used in these calculations.

The PE spectrum of the pyrolysate of **1** taken at a laser power level of 26 W, which corresponds to a temperature of 500 ± 50°C (3), is given in Fig. 1*b*. Besides nitrogen (sharp peak at 15.60 eV), the complex spectrum shows the prominent band of acetone (9.70 eV) (13). On its low-energy side, two bands of low intensity with maxima at 8.0 and 9.0 eV can be attributed to further pyrolysis products. One path of decomposition of oxadiazoline **1** is given in Scheme 1. If nitrogen and acetone are two products, the remaining PE spectrum must be partially due to dimethoxycarbene (**2**) or to products arising from **2**. When tetramethoxyethylene (**3**), the product of dimerization of **2**, was prepared (14) and its PE spectrum (Fig. 1*c*) recorded, the first low-intensity band in the pyrolysis spectrum of **1** could be assigned to **3** (first IP at 8.0, shoulder at 10.1, and maximum of the second band at 10.5 eV). Interesting is the very broad first band of **3**: its IP_a (first adiabatic ionization potential) is at 7.1 eV. Calculated Becke3LYP/6-31+G* first adiabatic and vertical IPs (Table 1) of the all-*anti* conformer, which is the global minimum according to HF/3-21G calculations, match experimental values and confirm the energy difference between IP_a and IP_v found in the spectrum. Upon opening the fast-pumping valve on the spectrometer in the thermolysis of **1**, the band at 8.0 eV disappeared, which is proof that **3** is formed through dimerization of **2**. To know whether **3** is stable at the thermolysis temperature (its thermal decomposition has been reported (15)), it was pyrolyzed in an independent experiment. The PE spectrum of the pyrolysate of **3** (not given) obtained at a laser power level of 26 W seems to be exclusively that of dimethyl oxalate (**4**) (16): IPs of bands are the same as those in a spectrum of an authentic sample of **4** taken with our spectrometer. The peak for the methyl radical (the literature value (17) is 9.84 eV) cannot be identified with certainty; it might be present on the low-energy side of the first band of **4**.

When the PE spectra of acetone, tetramethoxyethylene (**3**), and dimethyl oxalate (**4**) were subtracted from the pyrolysis spectrum of **1**, a simple spectrum remained. There are two bands of comparable intensity at 9.0 (onset at 8.4 eV) and 11.0 eV, followed by an unstructured region with its first band at 12.0 eV and a further maximum at 13.8 eV. These ionizations, except for the band at 12.0 eV, are reproduced nicely by Becke3LYP/6-31+G* calculations on dimethoxycarbene (**2**): for the *w* conformer given in Fig. 2(*b*), which is more stable than the *sk* conformer by 7.67 kJ mol^{-1} (or 7.64 kJ mol^{-1} when zero-point vibrational energies are included), IP_a and IP_v are 8.29 and 9.01 eV, respectively, and if orbital energies (−ε 6.36, 8.39, 9.97, and 10.34 eV) are shifted uniformly as explained above, the correlation is ideal (Fig. 1*d*). While data for the *sk* conformer are not too different, IP_a 8.11 eV, IP_v 9.01 eV, −ε 6.36, 8.71, 9.80, and 10.30 eV, a distinction between **2***w* and **2***sk* is possible by means of the second IP. The additional band at 12.0 eV is the only obvious ionization not arising from **2**. The facts that there are no bands unaccounted for in the low-energy region of the spectrum and that methyl radicals are being formed in the thermolysis of **3** led us to assign this band to ethane (literature (13) IP is 11.99 eV). Additional support for this is supplied by subtraction of the PE spectrum of **4** from the pyrolysis spectrum of **3**, which leaves a spectrum that has the features of that of ethane (13).

Neither were the products of a second possible path of decomposition of **1**, dimethylcarbene (and from it propene) and

dimethyl carbonate, detected in the pyrolysis PE spectrum, in agreement with results reported for the thermolysis of **1** in solution (9).

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