Selected Paper

Reaction of $(COCl)_2$ with AgN_3: Evidence for the Formation of Oxalyl Diazide $O_2C_2(N_3)_2$

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Oxalyl diazide $O_2C_2(N_3)_2$ has been generated in the heterogeneous reaction of $(COCl)_2$ vapor with AgN_3 at room temperature. Evidence for the formation of $O_2C_2(N_3)_2$ is based on on-line photoelectron spectroscopy (PES) characterization combined with the density functional B3LYP and outer valence Green's function (OVGF) calculations. The good agreement between the experimental spectra and theoretical calculation shows that $O_2C_2(N_3)_2$ has adiabatic ionization energy of 10.11 eV. Our results also suggest that $O_2C_2(N_3)_2$ has high conformational flexibilities and that the planar conformers are energy-favorable in gas phase.

Covalent azides have been known for more than 100 years.[1] Their chemistry has been attracting intense interest, not only owing to their widespread use as building blocks in organic and heterocyclic synthesis,[2–4] but also because of their potential for environmentally friendly high-energy density materials (HEDM).[5–7] In the family of covalent azides, oxalyl diazide ($O_2C_2(N_3)_2$) has been studied by Maier et al. as potential HEDMs and the precursor for highly-interesting OCN–NCO molecules.[8] But until now, the synthesis and properties of oxalyl diazide are still less known, due to its high explosiveness during preparation and handling. Hence, to find new applicable methods to generate this compound as well as to shed some light on the understanding of its properties, in this study, we reported the generation and characterization of oxalyl diazide by using photoelectron spectroscopy (PES) and quantum chemistry calculations.

Our laboratory has demonstrated the ability to generate continuously flowing beams of short-lived species[9–11] via the pyrolysis of suitable precursors, allowing us to perform PES studies combined with quantum chemistry calculations. Recently, our laboratory has been pursuing the preparation and characterization of azides and high-nitrogen content species.[12,13] During the preparation of thionyl azide $SO(N_3)_2$ from $SOCl_2$, it was found that AgN_3 is a good reagent to form covalent azides.[13] In this paper, we report the preparation of oxalyl diazide $O_2C_2(N_3)_2$ by the heterogeneous reaction between AgN_3 and $(COCl)_2$.

$$2AgN_3(s) + (COCl)_2(g) \rightarrow O_2C_2(N_3)_2(g) + 2AgCl(s). \quad (1)$$

The product of reaction (1) was examined in the PE spectrometer in combinations with theoretical calculations using density functional theory (DFT) and outer valence Green's function (OVGF) methods.

Experiment and Theoretical Methods

Caution. AgN_3 is highly explosive, especially as a pure dried-powder, so appropriate safety precautions should be taken.

Generation. $O_2C_2(N_3)_2$ is formed in the PE spectrometer by the heterogeneous reaction of $(COCl)_2$ vapor with freshly prepared AgN_3 at room temperature. Before experiment, the freshly prepared AgN_3 powder[14] was loosely filled into a quartz inlet tube and supported on quartz wool. $O_2C_2(N_3)_2$ is generated by passing $(COCl)_2$ vapor at a pressure of 1.0×10^{-3} torr over the freshly prepared AgN_3 at room temperature. At the initial stage of the reaction, the highly reactive AgN_3 powder was excessive, so the $(COCl)_2$ vapor passing through the inlet tube reacted completely with AgN_3 to produce $O_2C_2(N_3)_2$; in consequence, no signal of reactant was recorded on the PE spectrum. After about 30 min, the AgN_3 was used up then there appeared PE bands of $(COCl)_2$ on the spectrum.

PES Characterization. The PE spectrum of $O_2C_2(N_3)_2$ was recorded on a double-chamber UPS-II machine,[15] which was built specifically to detect transient species at a resolution of about 30 meV as indicated by the $Ar^+(^2P_{2/3})$ photoelectron band. Experimental vertical ionization energies (Iv in eV) are calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample.

$(COCl)_2$ was bought from the ACROS Company; its purity is better than 99.5%. The PE spectrum and first ionization energy (11.31 eV) of $(COCl)_2$ were the same as those reported.[16]

Theoretical Calculation. The equilibrium geometries and harmonic vibrational frequencies for the stable conformers and transition states of $O_2C_2(N_3)_2$ were located by density functional theory (DFT) calculations using Becke's three-parameter nonlocal exchange potential[17] with the nonlocal correlation of Lee, Yang, and Parr[18,19] (denoted as B3LYP in text) with the 6-31+G(d) basis sets. Their relative energies were calculated at B3LYP/6-311++G(3df) level plus the zero-point vibrational energy (ZPE)

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corrections with the 6-31+G(d) basis sets to confirm their conformational stabilities.

In order to assign PE bands of the $O_2C_2(N_3)_2$, outer valence Green's function (OVGF) calculations[20] which include the effect of electron correlation and reorganization were carried out for all conformers to get their vertical ionization energy (E_v) and molecular orbital coefficients corresponding to each PE band. This method has been successfully applied to a fairly large number of molecules and high accuracy can be achieved. In addition, the E_v values were also calculated at B3LYP/6-311++G(3df) level from the difference of the total energies of the resulting cation/neutral species of $O_2C_2(N_3)_2$. All above calculations were performed using Gaussian 98 Program.[21]

Results and Discussion

Though the geometric and conformational properties of the dicarboxylic compounds (such as oxalic acid,[22–24] oxalyl chloride,[25,26] etc.) have been extensively studied, to the best of our knowledge, neither experimental results nor theoretical structures for oxalyl diazide have been reported. The geometries of $O_2C_2(N_3)_2$ were optimized using the B3LYP method with 6-31+G(d) basis sets: four planar conformers (denoted as *a*–*d*) and a *gauche*-conformer (conformer *e*) were obtained. Their geometric parameters and relative energies calculated at B3LYP/6-311++G(3df) level plus the zero-point vibrational energy correlation are listed in Fig. 1.

The stabilities of five conformers of $O_2C_2(N_3)_2$ are in following sequence: $a > d > b > c > e$, the global minimum is the planar conformer *a* with C_{2h} symmetry, where the two carboxyl groups are in *trans*-position and both azido groups are also in *trans*-positions to the C_1–C_2 bond. The sole nonplanar one, conformer *e*, is least stable. That is, in gas phase the molecule favors planar conformers in which the formation of delocalized π orbitals decrease the total energy of molecule and makes it more stable. It is found that the energy differences among these conformers are quite small (within 5 kcal/mol); this implies that the molecule has high rotational flexibilities and all rotamers may make contributions to the total conformational space of gaseous $O_2C_2(N_3)_2$.

The rotational isomerizations mechanism of $O_2C_2(N_3)_2$ is also suggested in Fig. 1. Rotating along the C–C or C–N single bonds, the five conformers can change their conformations along five pathways, corresponding to five rotational transition states, denoted as T_{ab}, T_{ad}, T_{bc}, T_{be}, and T_{de}, respectively. Their geometries as well as the harmonic vibrational frequencies were calculated at B3LYP/6-31+G(d) level; the relative energies, obtained by using same method with the 6-311++G(3df) basis sets plus ZPE correlation, are shown in Fig. 1. As a whole, the rotational barriers of gaseous $O_2C_2(N_3)_2$ are relatively low and are easily surmountable by the thermal motion. It is also found that the internal rotations around C–C bonds have lower barrier while rotations around the C–N bond have significantly high barriers, suggesting that the singly occupied p orbital on carbon overlaps more effectively with the lone pair on nitrogen (i.e. the π orbital within the azido group) than with the p orbital on the other carbon. In fact, the interactions between azido and carbonyl groups have a vital influence on the PE spectra of such compounds; the interactions could act as one of the most important factors in assigning and interpreting the PE bands.

Figure 2 gives the PE spectrum of the product obtained by the heterogeneous reaction of $(COCl)_2$ vapor at a pressure of 1.0×10^{-3} torr with AgN_3 at room temperature.

To our knowledge, the photoelectron spectroscopic study of dicarbonyl compounds has attracted extensive attention during the past thirty-years and therefore has a very long history go-

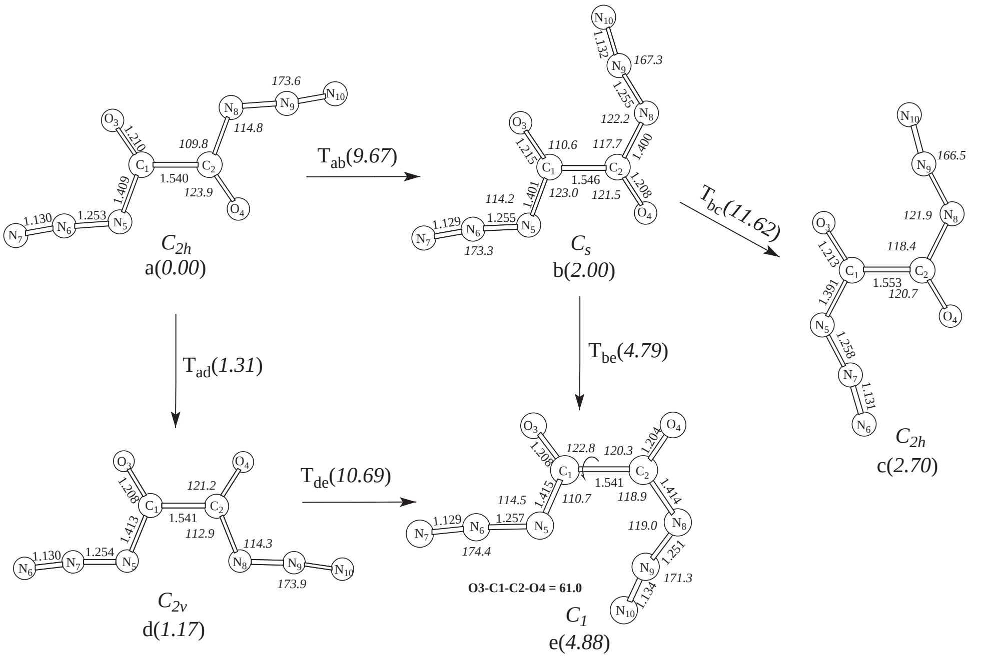

Fig. 1. Optimized geometric parameters (bond lengths in Å and angles in °) and relative energies (in kcal/mol, plus zero-point vibrational energy) as well as the schematic rotational isomerizations mechanism (T denotes the relative energy of transition state) for five conformers (*a*–*e*) of oxalyl diazide.

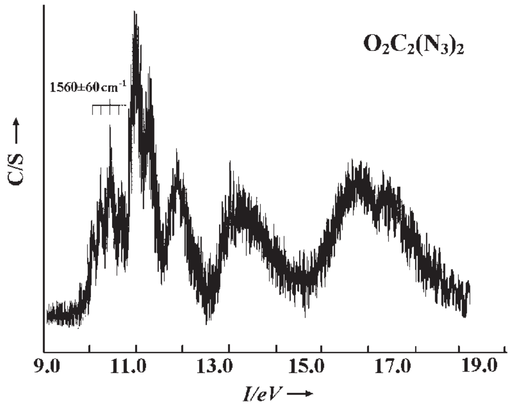

Fig. 2. A complete HeI photoelectron spectrum (PES) of $O_2C_2(N_3)_2$.

ing back to the work of McGlynn et al.[27,28] The orbital structures and through-space interactions of substituted dicarbonyls have been thoroughly discussed and some fundamental rules were established, which may act as baselines during our assignment of the PE spectra of oxalyl diazide.

The assignment of the observed PE spectrum of $O_2C_2(N_3)_2$ is also supported by theoretical calculations of ionization potential and their corresponding orbital characters as well as the vibrational spacing of the neutral and cationic states. As mentioned above, the structures of $O_2C_2(N_3)_2$ in gas phase are not unique, so all the conformers were considered in the calculations of ionization energies. The experimental vertical ionization energies (IP in eV), ionization energies (E_v in eV) computed by using OVGF and DFT-B3LYP approaches with a 6-311++G(3df) basis set as well as the corresponding molecular orbital characters for $O_2C_2(N_3)_2$ are listed in Table 1.

From Table 1, good agreements were found between the experimental and theoretical ionization energies, as well as good consistency between the band-shapes of PE spectra and theoretical predicted MO characters. These provide evidence that the new compound obtained from the heterogeneous reaction of $(COCl)_2$ and AgN_3 at room temperature is $O_2C_2(N_3)_2$.

The first PES band with vibrational spacing of 1560 ± 60 cm^{-1} is assigned to the ionization of the electron from the highest occupied molecular orbital (HOMO) (orbital 35) in the $O_2C_2(N_3)_2$ molecule. It is seen from Table 1 the OVGF-calculated first vertical ionization energies, varying from 10.546 to 10.811 eV, are slightly larger and the DFT calculated values are slightly lower; both are comparable to the experimental value 10.50 eV. On the other hand, both our OVGF and B3LYP calculations show the HOMOs are largely localized on the oxygen center of the carbonyl group, corresponding to the characters of a localized "in-plane" $n_{O(C=O)}$ anti-bonding orbital. Ionization of this orbital should be accompanied by a distinct change in molecular geometry in the cationic state; therefore, a band with predominantly carbonyl vibration should be clearly observed. Fortunately, the vibrational spacing observed here, 1560 ± 60 cm^{-1}, is similar to that for compounds containing carbonyl groups (~1400–1600 cm^{-1}).[29,30] To better interpret the MO character, we give three-dimensional contour plots (contour value = 0.05) of the HOMOs and SHOMOs for the conformers of $O_2C_2(N_3)_2$ in Fig 3.

Furthermore, ionization of the "in-plane" $n_{O(C=O)}$ orbital should lead to a band in which the adiabatic and vertical ionizations are not coincident. The adiabatic ionization energy of $O_2C_2(N_3)_2$, 10.11 eV—differing from its vertical ionization energy of 10.50 eV—can also obtained from the PE spectra.

The second peak at 10.98 eV corresponds to ionization of the electron from the second HOMO (SHOMO) (orbital 34), which is largely localized on the substituent N_3 groups in the $O_2C_2(N_3)_2$ molecule (see Fig. 3, second row). This assignment is not only based on the energetic similarity between the experimental value and the computed ionization ones, but also due to the sharp and intensive band-shape, which is in good agreement with the one caused by the theoretical calculated "out-of-plane" anti-bonding π_{N-N-N} coefficients.

The third sharp peak at 11.22 eV is very similar to the second one; it corresponds to the orbital 33 with the dominant contribution from the N_3 groups. In fact, the second and third peaks come from the ionization of a pair of zero-order degenerate "out-of-plane" π orbitals. This degeneracy is removed by interactions with the carbon skeleton; as a result, the two peaks break apart with an interval about 0.25 eV.

Table 1. Experimental Vertical Ionization Energies (IP in eV), Computed Ionization Energies (E_v in eV) by OVGF and B3LYP (in Parentheses) Calculations with the 6-311++G(3df) Basis Sets as well as the Corresponding Orbital Characters for Five Conformers (*a*–*e*) of $O_2C_2(N_3)_2$

IP/eV	E_v/eV					MO	Character[a)]
	a	*b*	*c*	*d*	*e*		
10.50	10.628	10.681	10.546	10.780	10.811	35	$n_{O(C=O)}$(i)
(10.11, 10.30, 10.50, 10.69, 10.89)	(10.123)	(10.230)	(10.295)	(10.545)	(10.351)		
10.98	10.822	10.715	10.910	11.120	10.900	34	π_{N-N-N}(o)
11.22	11.066	11.178	11.010	11.121	11.254	33	π_{N-N-N}(o)
11.97	12.233	12.290	12.550	11.503	12.354	32	π_{N-N-N}(i)
13.11	13.047	12.799	12.842	13.337	12.838	31	π_{N-N-N}(i)
	13.639	13.677	13.368	13.432	13.959	30	$n_{C=O}$(i)
14.42	14.361	14.399	14.626	14.230	14.729	29	$\pi_{C=O}$
15.70	15.787	15.770	15.853	15.712	15.403	28	$\pi_{C=O}$, π_{C-C}
16.39	16.442	16.069	16.010	16.443	16.361	27	σ_{C-O}

a) The character MO being ionized, where (i) denotes "in-plane" molecular orbital while (o) represents "out-of-plane" orbitals which are perpendicular to the molecular framework.

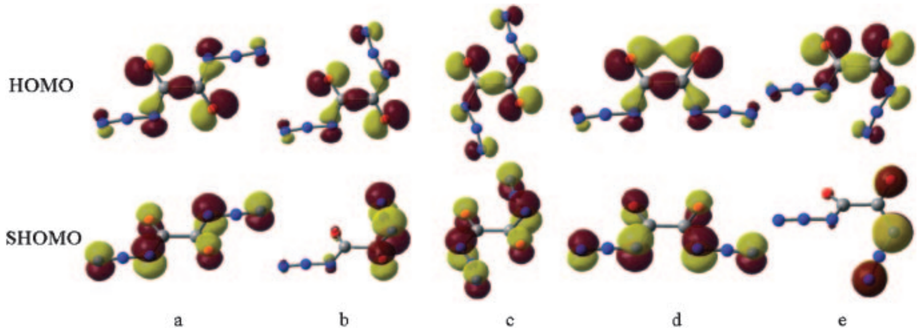

Fig. 3. Characters of the highest occupied molecular orbitals (HOMOs, first row) and second-HOMOs (SHOMOs, second row) for five conformers of oxalyl diazide.

During the analysis of the corresponding MO characters of the second and third band, some interesting points were found. In the high symmetric conformers (such as *a*, *c*, and *d*, with C_{2h}, C_{2h}, and C_{2v} symmetry, respectively), both azido groups make equal contributions to the total MO coefficients of SHOMO (orbital 34) and orbital 33, but the interactions between N_3 groups and carbon skeleton force the degenerate orbitals to divide into two energy levels; therefore, the electrons ionized from these two orbitals lead to two different but similar PE bands. In the low symmetric conformer including conformers *b* (C_s) and *e* (C_1), the second PE band results from the ionization of SHOMO with dominant character of the azido group (N_8–N_9–N_{10}), which is in *cis*-position to the central C–C skeleton; the third band has the main character of another N_3 group (N_5–N_6–N_7) in *trans*-position to C–C bond. Both of them could interpret the observed PE bands so we did not make any further effort to distinguish them.

The fourth PES band centered near 11.97 eV and the fifth one located near 13.11 eV are assigned to the ionization of orbital 32 and 31, which have the dominant characters of "in-plane" π coefficients in N_3 groups. But the fifth band seems much broader than the former one, so it may imply that the fifth band embodied more than a single orbital.

According to the empirical rules of dicarbonyl compounds[28] as well as our calculation results, there should exist another broad PE band in the high ionization energy region which has almost the same coefficients as the first PE sharp band at 10.50 eV, that is, the "in-plane" $n_{O(C=O)}$ orbital localized at carbonyl groups. The theoretical predicted region varying from 13.4 to 14.0 eV, falls over the fifth band starting from 13.11 eV. In fact, the uncommon over-broad band-shape of the fifth band is caused by overlap of these two peaks. Due to its low intensity and heavy overlap, the precise ionization potential of the sixth peak is hard to measure.

The PES bands in the high ionization energy region (>14.00 eV) exhibit broad bands, which result from the ionization of the electrons of the deep orbitals. These bands are composed from several individual peaks overlapping each other, so only their ionization potential and MO characters are given, without further interpretations.

An X-ray diffraction analysis shows that the solid residue in the reactor inlet tube is AgCl(s).[31] This fact further supports the conclusion that the heterogeneous reaction of $(COCl)_2$ vapor with AgN_3 leads to the formation $O_2C_2(N_3)_2$.

Conclusion

In summary, the preparation of oxalyl diazide $O_2C_2(N_3)_2$ has been realized. The new compound has been characterized by a combination of PES characterization with theoretical calculations. The good agreement between the calculated and experimental PES shows that $O_2C_2(N_3)_2$ has adiabatic ionization energy of 10.11 eV. Furthermore, $O_2C_2(N_3)_2$ has high conformational flexibilities and the planar conformers are energy-favorable in gas phase.

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