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## Propinal O-oxide

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### Abstract

Propinal O-oxide has been generated by the thermal reaction of propargylene and molecular oxygen under the condition of matrix-isolation in O<sub>2</sub>-doped argon matrices. The carbonyl oxide and several products of its photolysis have been characterized using IR and UV-VIS spectroscopy. The infrared spectrum has been calculated using ab initio calculations at the QCISD/6-31G(d, p) level of theory. There is a good agreement between experimental and calculated IR data for the *s*-Z isomer of the carbonyl oxide and some evidence for the formation of smaller amounts of the *s*-E isomer. Thus, experimental and high-level ab initio data of a carbonyl oxide can be compared directly and geometrical isomers distinguished.

### 1. Introduction

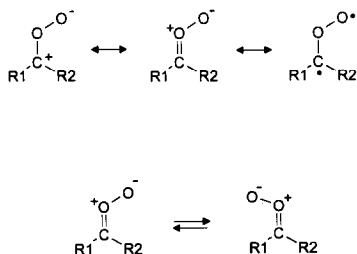
Carbonyl O-oxides and the isomeric dioxiranes have attracted considerable interest from both theoretical and experimental points of view [1]. Carbonyl oxides, the so-called 'Criegee zwitterions', have been detected as products of the thermal reaction of carbenes with oxygen, e.g. by means of time-resolved laser flash photolysis methods [2], or by IR and UV-VIS spectroscopy at low temperatures [3]. Carbonyl oxides are key intermediates in the ozonolysis of olefins [4], but so far they have never been observed directly in an ozonolysis reaction [5]. The only practicable route to the spectroscopic detection of carbonyl oxides is the oxidation of diazo compounds with <sup>1</sup>O<sub>2</sub> or of carbenes with <sup>3</sup>O<sub>2</sub> [2,3]. In contrast to the short-lived carbonyl oxides, the preparative scale synthesis of comparatively stable dioxiranes has been reported [6,7], and dimethyl dioxirane is now widely used as an oxidizing agent [7].

The electronic structure of a carbonyl oxide may

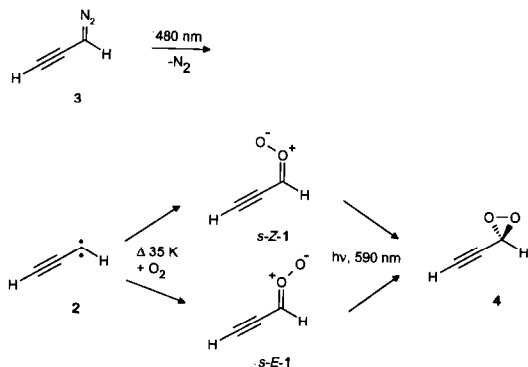
be described in terms of a zwitterion, a biradical, or polar biradicaloid structures between these two extremes. Theoretical work on a semi-empirical level showed that some carbonyl oxides are well-described as singlet biradicals [8], but high-level ab initio theory questions this assignment [9–13]. An example is the calculated equilibrium structure and the corresponding infrared spectrum of the parent compound, formaldehyde O-oxide, which was investigated by Cremer and co-workers. The bond lengths of the COO moiety differ significantly at the CCSD(T) level compared to the MP2/6-31G\* level of theory [3,11]. At the CCSD(T) level, the diradical character of the molecule is calculated to be much less important. As a consequence, the calculated frequencies of the  $\nu_{C=O}$  and  $\nu_{O-O}$  vibrations are shifted (in opposite directions) by about 100 cm<sup>-1</sup>.

If carbonyl oxides are substituted asymmetrically, *s*-E and *s*-Z geometrical isomers can exist. Two pathways for the E/Z isomerization have to be considered: rotation around the C–O bond and inversion at

an oxygen atom with a linear C–O–O transition state. For the parent carbonyl oxide the activation barriers for these processes have been calculated to be 32.1 and 42.2 kcal/mol, respectively, using second-order RSMP perturbation theory [13]. The barrier for the cyclization to dioxirane has been estimated to 19.2 kcal/mol at the CCSD(T) level [12]. At cryogenic temperatures even a shallow activation barrier (>2 kcal/mol) should be sufficient to inhibit E/Z isomerization completely. However, the spectroscopic characterization of distinct geometrical isomers of carbonyl oxides relies on accurate calculations of the IR spectra and therefore has not been possible for carbonyl oxides with larger substituents.



To allow a comparison with high level ab initio data the carbonyl oxides in question have to be rather small molecules. Unfortunately, most small carbonyl oxides such as acetaldehyde O-oxide or acetone O-oxide cannot be prepared by carbene oxidation, since the corresponding carbenes undergo rapid 1,2-hydrogen migrations. Here, we report on the matrix isolation of propinal O-oxide 1, which is a molecule small enough to be subjected to high level ab initio calculations. Also, this study provides evidence for the preferential formation of one single isomer (presumably *s-Z*) in the thermal reaction of triplet propargylene 2 and oxygen in argon matrices at 32 K,



## 2. Results and discussion

Propargyldiazomethane 3 was prepared from N-nitroso-N-propargylurea following the method of Maier et al. [14,15] (caution: the diazo compound is highly explosive and violently detonated twice in our laboratory). Diazo compound 3 was sublimed at  $-110^{\circ}\text{C}$  and co-deposited with argon/oxygen mixtures on a spectroscopic window. To obtain optically clear matrices the spectroscopic window was kept at 28–30 K during deposition and after that cooled to 10 K. Irradiation ( $\lambda=480\pm 20\text{ nm}$ ) of 3, matrix isolated in 1.2%–1.5% oxygen-doped argon at 10 K, produced propargylene 2,  $\text{CO}_2$ , CO, propiolic acid, propinal, traces of cyclopropanone ( $1815\text{ cm}^{-1}$ ), but no ketene or propadienone. Upon annealing at 30–35 K for several minutes the matrix turned yellow, and new infrared absorptions which we assign to the propinal O-oxide 1 appeared, concomitant with the decay of carbene 2 (Fig. 1). After one hour the reaction came to a halt although some carbene still remained in the matrix. Irradiation of the yellow matrix with  $\lambda\geq 590\text{ nm}$  let the matrix turn colorless and destroyed the IR absorptions assigned to 1. The photoproducts were

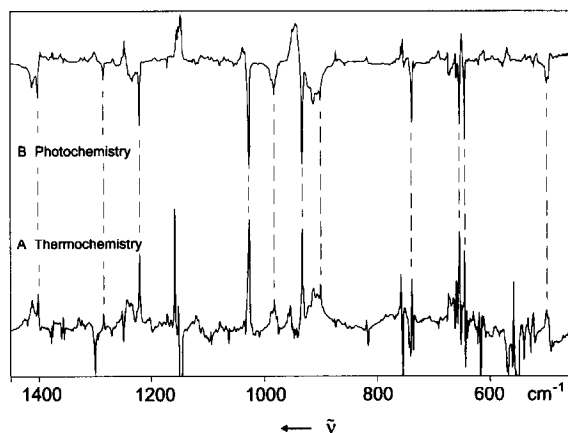


Fig. 1. Difference IR spectra in absorbance, IR bands pointing downwards are decreasing in intensity (assigned to reactants), IR bands pointing upwards are increasing (assigned to products). (A) Changes on annealing a 1%  $\text{O}_2$ -doped argon matrix containing propargylene 2 at 32 K for several minutes. IR bands pointing downwards are assigned to carbene 2, IR bands pointing upwards to the products of oxidation, mainly 1. (B) Photochemistry of propinal O-oxide (same matrix as (A), irradiation with  $\lambda=590\text{ nm}$ ). IR bands pointing downwards assigned to 1, IR bands pointing upwards to the products of the photolysis, mainly dioxirane 4.

identified as CO, propinal, and a further product with a set of weak bands <sup>#1</sup> tentatively assigned to propargyl dioxirane **4**. The dioxirane decayed on irradiation with  $\lambda=403\pm 20$  nm to give mainly CO<sub>2</sub>, propiolic acid and acetylene.

In view of the deficiencies of the MP2 method in the case of carbonyl oxides, the geometries and infrared spectra of the E- and Z-isomers of **1** were calculated at the coupled cluster level of theory using QCISD/6-31G(d, p) <sup>#2</sup> (Table 1 and Fig. 2). In addition, we have carried out CCSD(T)/DZ+P [17] geometry optimizations on **1** in order to assess from calculated geometries (Fig. 2) possible shortcomings of a coupled cluster description that does not include triple excitations. The latter have been found to be

essential for the correct description of the infrared spectrum of H<sub>2</sub>COO [12], but a QCISD(T) or CCSD(T) calculation of the infrared spectrum of **1** is not feasible at the moment <sup>#3</sup>.

At all levels of theory the Z-form of **1** is slightly more stable (QCISD:  $\Delta H=0.5$  kcal/mol; CCSD(T):  $\Delta H=0.3$  kcal/mol <sup>#4</sup>) than the E-form, which is a result of favourable through-bond interactions in the first case [19]. The geometries of the two isomers hardly differ, both being characterized by CO and OO bond lengths typical of a carbonyl oxide (Fig. 2) [12]. QCISD describes qualitative features of the carbonyl oxide unit correctly, but differs by 1–3 pm and 1–2° from the more reliable CCSD(T) geometry, which has to be considered with regard to calcu-

<sup>#1</sup> Propargyl dioxirane **4** (Ar, 10 K): 3319 (0.999), 1397 (0.990), 1375 (-), 1247 (0.981), 950 (0.997), 873 (0.970), 676 (1.000) cm<sup>-1</sup> ( $\nu_i/\nu$  on <sup>18</sup>O labelling).

<sup>#2</sup> QCISD and QCISD(T): see ref. [16].

<sup>#3</sup> All calculations have been performed with the program ACES II [18].

<sup>#4</sup> Enthalpy differences have been obtained using vibrational corrections calculated at the QCISD/6-31G(d, p) level of theory.

Table 1  
Calculated and experimental IR data of propinal O-oxide **1**

No.	<i>s</i> -E- <b>1a</b> (QCISD/6-31G(d, p))				<i>s</i> -Z- <b>1b</b> (QCISD/6-31G(d, p))				<i>s</i> -Z- <b>1b</b> (exp., Ar, 10 K)		
	$\nu^a$ (cm <sup>-1</sup> )	<i>I</i> (km/mol)	$\nu_i/\nu^b$	description	$\nu^a$ (cm <sup>-1</sup> )	<i>I</i> (km/mol)	$\nu_i/\nu^b$	description	$\nu$ (cm <sup>-1</sup> )	rel. int.	$\nu_i/\nu^b$
1	158	0.1	0.965	skeletal o.o.p.	150	4.0	0.982	skeletal bend			
2	168	1.5	0.984	skeletal bend	229	1.1	0.980	skeletal o.o.p.			
3	369	4.9	0.995	skeletal o.o.p.	334	4.2	0.976	skeletal bend			
4	419	9.9	0.967	skeletal bend	420	3.6	0.984	skeletal o.o.p.	497.1	w	0.982
									500.4		
5	539	3.1	0.978	skeletal bend	585	45.7	1.000	C1H1 o.o.p.	646.5	m	1.000
6	575	45.4	1.000	C1H1 o.o.p.	593	33.3	0.999	C2C1H1 bend	655.6	m	1.000
7	625	38.7	1.000	C2C1H1 bend	693	16.7	0.968	C2C3O1 bend	739.0	m	0.970
8	795	4.7	0.997	C3H2 o.o.p.	729	3.9	1.000	C3H2 o.o.p.			
9	1012	51.7	0.974	C2C3 stretch, C2C3O1 bend	933	s*	0.965	OO stretch	933.3	s	0.952
10	1046	7.9	0.978	OO stretch + COO bend	1012	49.6	0.991	C2C3 stretch, C2C3O1 bend	1026.4	s	0.993
11	1249	15.1	0.976	CO+OO stretch	1210*	16.6	0.973	CO stretch	1221.2	m	0.981
12	1416	49.8	0.988	H2C3O1 bend	1413	69.8	0.991	H2C3O1 bend	1401.5	m	0.995
13	2087	42.4	1.000	C=C stretch	2076	72.7	1.000	C=C stretch	2093.8	s	1.000
									2098.6		
14	3114	0.4	1.000	C3H2 stretch	3128	2.3	1.000	C3H2 stretch	- <sup>c</sup>		
15	3345	59.9	1.000	C1H1 stretch	3345	45.4	1.000	C1H1 stretch	3313.5	s	1.000

<sup>a</sup> QCISD frequencies have been scaled by 0.95. Values with asterisks have been obtained by using QCISD and CCSD(T) spectrum of carbonyl oxide [12] as reference (see text).

<sup>b</sup> Shift upon <sup>18</sup>O-substitution. <sup>c</sup> Assignment not possible.

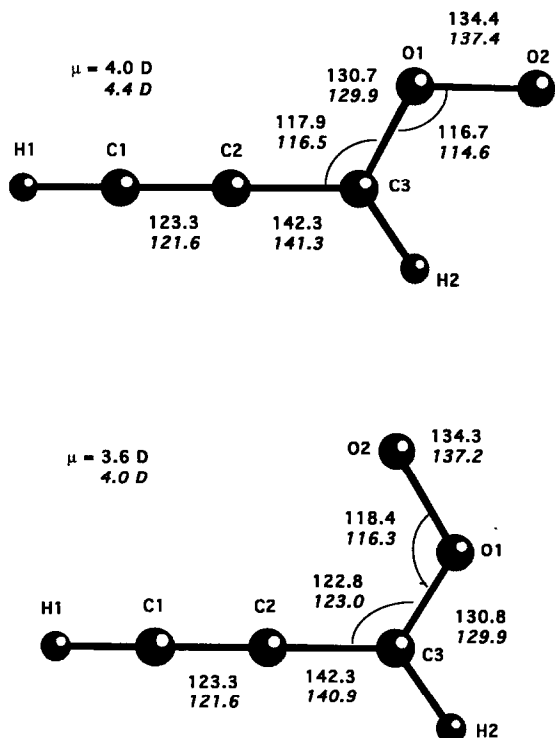


Fig. 2. Calculated equilibrium geometries of the geometrical isomers of propinal O-oxide 1. Top: *s*-E-isomer 1a. Bottom: *s*-Z-isomer 1b. CCSD(T)/DZ+P bond lengths (pm) and bond angle (deg) in normal print, QCISD/6-31G(d, p) values in italics.

lated QCISD infrared spectra.

A comparison of experimental and calculated infrared spectra (Table 1) suggests that the former is dominated by one isomer since the small number of strong infrared bands cannot account for two isomers. From previous experience we know that QCISD describes the vibrational modes of carbonyl oxide qualitatively correctly but, compared to the more correct CCSD(T) method, overestimates frequencies and underestimates intensities of the CO and OO stretching modes. Analysis of the normal modes of 1 reveals that a clear assignment of the CO and OO stretching vibrations and a calibration with reference data from carbonyl oxide are only possible in the case of the QCISD spectrum of *s*-Z-1 (see Table 1).

The calibrated QCISD spectrum of *s*-Z-1 agrees well with the measured infrared spectrum shown in Fig. 3, while the QCISD spectrum of *s*-E-1 does not. However, there are weak and broad absorptions at 1412, 1234, 983 and 914  $\text{cm}^{-1}$ , which according to calculations can be tentatively assigned to the E isomer of 1. Another weak band at 1285  $\text{cm}^{-1}$  is supposed to be an overtone of the vibration at 655  $\text{cm}^{-1}$  since neither Z nor E isomer absorb in this region nor does the band in question change upon  $^{18}\text{O}_2$  substitution.

The identification of *s*-Z-1 is best performed by the OO stretching mode at 933  $\text{cm}^{-1}$  (QCISD: 933, Table 1), the CO stretching mode at 1221  $\text{cm}^{-1}$  (QCISD

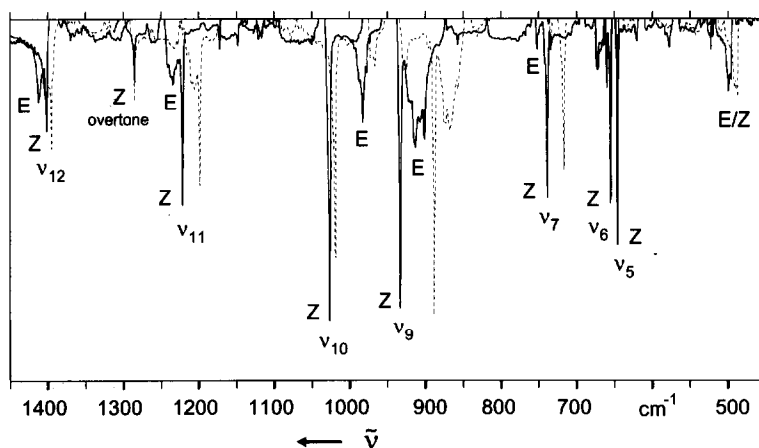


Fig. 3. IR spectrum of propinal O-oxide 1 in 1%  $\text{O}_2$ -doped argon at 10 K. 1 has been produced by annealing the matrix containing propargylene 2 at 32 K for several minutes. The difference IR spectrum shows only the products formed during the warm-up experiment. Dotted lines correspond to the spectrum produced by using  $^{18}\text{O}_2$ . The assignment of bands to *s*-Z-1 is based on the QCISD/6-31G(d, p) infrared spectra (Table 1). Several broad absorption are tentatively assigned to *s*-E-1.

corrected:  $1210\text{ cm}^{-1}$ ). Both bands show relatively strong isotope shifts (exp. 45 and  $23\text{ cm}^{-1}$ ; QCISD 33 and  $37\text{ cm}^{-1}$ , Table 1 and dotted lines in Fig. 3) upon  $^{18}\text{O}_2$  substitution. The bands tentatively assigned to *s*-E-1 are at somewhat higher wave numbers (OO: exp. 983, QCISD 1046; CO: exp. 1234, QCISD  $1250\text{ cm}^{-1}$ ), which results from the involvement of other atoms in the vibrational modes.

The relative intensities of the infrared bands of *s*-Z-1 and *s*-E-1 suggest that there is a considerable amount of the latter form in the reaction mixture. Under the assumption of an equilibrium between the two forms at 30 K an energy difference of 0.3 kcal/mol would shift the equilibrium totally to the side of the *s*-Z-form. However, it is more likely that the distribution of isomers in the infrared probe is determined by energy differences in the transition states of the formation reaction and these will be much smaller than 0.3 kcal/mol if the transition state is located in the entrance channel of the strongly exothermic reaction.

Attempts to oxidize the other two (singlet)  $\text{C}_3\text{H}_2$  carbene isomers, vinylidene carbene and cyclopropylidene, which were generated photochemically from propargylene as described by Maier et al. [14,20], were unsuccessful. Both compounds were stable to conditions under which triplet **2** was rapidly oxidized, and even upon irradiation no significant photooxidation occurred.

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### References

- [1] S.A. Kafafi, R.I. Martinez and J.T. Herron, *Mol. Struct. Energ.* 6 (1988) 283;
- R.L. Kuczkowski, in: 1,3-dipolar cycloaddition chemistry, Ozone and carbonyl oxides, ed. A. Padwa (Wiley, New York, 1984) ch. 11;
- W. Sander, *Angew. Chem.* 102 (1990) 362; *Angew. Chem. Intern. Ed. Engl.* 29 (1990) 344;
- W.H. Bunnelle, *Chem. Rev.* 91 (1991) 335;
- R.L. Kuczkowski, *Chem. Soc. Rev.* (1992) 79.
- [2] H.L. Casal, S.E. Sugamori and J.C. Scaiano, *J. Am. Chem. Soc.* 106 (1984) 7623.
- [3] G.A. Bell, I.R. Dunkin, *J. Chem. Soc. Chem. Commun.* (1983) 1213;
- I.R. Dunkin and G.A. Bell, *Tetrahedron* 41 (1985) 339;
- G.A. Bell, I.R. Dunkin and C.J. Shields, *Spectrochim. Acta Part A* 41 (1985) 1221;
- G.A. Ganzer, R.S. Sheridan and M.T.H. Liu, *J. Am. Chem. Soc.* 108 (1986) 1517;
- W. Sander, *J. Org. Chem.* 54 (1989) 333;
- S. Murata, H. Tomioka, T. Kawase and M. Oda, *J. Org. Chem.* 55 (1990) 4502;
- G. Bucher and W. Sander, *Chem. Ber.* 125 (1992) 1851.
- [4] R. Crigee, *Angew. Chem.* 87 (1975) 765;
- Y. Fujiwara, Y. Tanimoto, M. Itoh, K. Hirai and H. Tomioka, *J. Am. Chem. Soc.* 109 (1987) 1942;
- T. Sugawara, H. Iwamura, H. Hayashi, A. Sekiguchi, W. Ando and M.T.H. Liu, *Chem. Letters* (1983) 1261;
- M.T.H. Liu, R. Bonneau and C.W. Jefford, *J. Chem. Soc. Chem. Commun.* (1990) 1482;
- S. Morgan, M.S. Platz, M.J. Jones and D.R. Myers, *J. Org. Chem.* 56 (1991) 1351;
- B.R. Arnold, J.C. Scaiano, G.F. Bucher and W. Sander, *J. Org. Chem.* 57 (1992) 6469.
- [5] D. Cremer, E. Kraka, M.L. McKee and T.P. Radhakrishnan, *Chem. Phys. Letters* 187 (1991) 491.
- [6] A. Russo and D.D. DesMarteau, *Angew. Chem.* 105 (1993) 956; *Angew. Chem. Intern. Ed. Engl.* 32 (1993) 905.
- [7] W. Adam and L. Hadjarapoglou, *Topics Current Chem.* 164 (1993) 45;
- R.W. Murray, *Chem. Rev.* 89 (1989) 1187.
- [8] L.A. Hull, *J. Org. Chem.* 43 (1987) 2780;
- D. Cremer, T. Schmidt, W. Sander and P. Bischof, *J. Org. Chem.* 54 (1989) 2515.
- [9] D. Cremer, T. Schmidt, J. Gauss and T.P. Radhakrishnan, *Angew. Chem.* 100 (1988) 431; *Angew. Chem. Intern. Ed. Engl.* 27 (1988) 427.
- [10] J. Gauss and D. Cremer, *Chem. Phys. Letters* 133 (1987) 420.
- [11] S.D. Kahn, W.J. Hehre and J.A. Pople, *J. Am. Chem. Soc.* 109 (1987) 1871.
- [12] D. Cremer, J. Gauss, E. Kraka, J.F. Stanton and R.J. Bartlett, *Chem. Phys. Letters* 209 (1993) 547.
- [13] D. Cremer, *J. Am. Chem. Soc.* 101 (1979) 7199.
- [14] G. Maier, H.P. Reisenauer, W. Schwab, P. Carsky, V. Spirko, B.A.J. Hess and L.J. Schaad, *J. Chem. Phys.* 91 (1989) 4763.
- [15] F.K. Chi, *Vibrational spectra of diazopropylene and its photolysis product: the propargylene radical*, Ph.D. Thesis, Michigan, State University (1972).

- [16] J.A. Pople, M. Head-Gordon and K.J. Raghavachari, *Chem. Phys.* 87 (1987) 5968;  
J. Gauss and D. Cremer, *Chem. Phys. Letters* 150 (1988) 280; *Chem. Phys. Letters* 153 (1989) 303.
- [17] K. Raghavachari, G.W. Trucks, J.A. Pople and M. Head-Gordon, *Chem. Phys. Letters* 157 (1989) 479;  
R.J. Bartlett, J.D. Watts, S.A. Kucharski and J. Noga, *Chem. Phys. Letters* 165 (1990) 513.
- [18] J.F. Stanton, J. Gauss, J.D. Watts, W.J. Lauderdale and R.J. Bartlett, ACES II, Quantum Theory Project, University of Florida (1992).
- [19] R. Hoffmann, A. Imamura and W.J. Hehre, *J. Am. Chem. Soc.* 90 (1968) 1499;  
T.A. Albright, J.K. Burdett and M.H. Whangbo, *Orbital interactions in chemistry* (Wiley, New York, 1985).
- [20] H.P. Reisenauer, G. Maier, A. Riemann and R.W. Hoffmann, *Angew. Chem.* 96 (1984) 596; *Angew. Chem. Intern. Ed. Engl.* 23 (1984) 641;  
G. Maier, H.P. Reisenauer, W. Schwab, P. Carsky, B.A.J. Hess and L.J. Schaad, *J. Am. Chem. Soc.* 109 (1987) 5183.