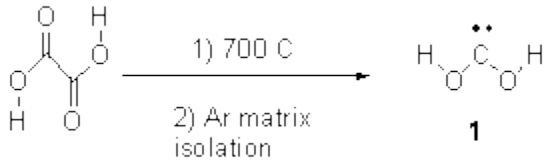
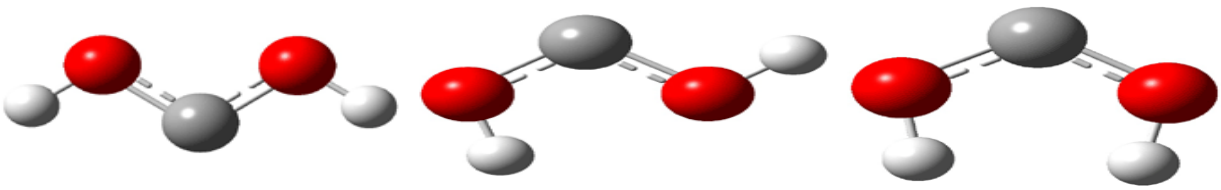
DIHYDROXYCARBENE

Following on the great study of hydroxycarbene[1], Schreiner now reports on the synthesis and characterization of dihydroxycarbene **1**.[2] It is prepared by high-vacuum flash pyrolysis of oxalic acid (Scheme 1).

Scheme 1



Dihydroxycarbene can exist in three different conformations characterized by the relationship about the C-O bond, either *s-cis* or *s-trans*. The three conformations are shown in Figure 1, and the *s-trans,s-trans* structure is the local energy minimum (computed at CCSD(T)/cc-pVTZ).



1tt (0.0) **1ct** (0.1) **1cc** (6.7)

Figure 1. CCSD(T)/cc-pVTZ optimized geometries and relative energies (kcal mol^{-1}) of the conformers of **1**.[2]

Identification of the **1** is made through comparison of the experimental and computed IR vibrational frequencies. As an example, the experimental and computed frequencies for the *s-trans,s-trans*conformer are listed in Table 1. The agreement is excellent.

Table 1. Computed and experimental vibrational frequencies (cm^{-1}) and intensities (in parentheses) of the *s-trans,s-trans* conformation of **1**.[2]

vibration	computed	experiment
1	3876.4 (23.5)	3633.2 / 3628.6 (w)
2	3871.4 (234.1)	3625.1 (s)
3	1443.1 (124.4)	1386.2 (m)
4	1370.5 (58.3)	1289.0 / 1287.4 (w)
5	1157.8 (470.6)	1110.3 / 1109.3 (vs)
6	1156.6 (1.4)	
7	742.4 (178.8)	706.6 (s)
8	672.4 (0.0)	
9	641.6 (11.2)	

Unlike hydroxycarbene, dihydroxycarbene is stable. The amazing instability of hydroxycarbene is due to tunneling through a large barrier: nearly 30 kcal mol^{-1}.[1,1] The tunneling route for the decomposition of **1** is more difficult for two reasons. First, its C-O bond is quite strong; the C-O distance is quite short, 1.325 Å. This makes a long distance that must be traversed in the tunneling mode. (The strong bond is due to π-donation from the oxygen lone pair into the empty carbon *p*orbital; this is noted by the large rotational barrier about the C-O bonds of 17 kcal mol^{-1}!) Second, the activation barrier for decomposition is very high, at least 34 kcal mol^{-1}.

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