A Reinvestigation of the Fragmentation of 2-Carbena-1,3-dioxolane by CASSCF and CASPT2 Calculations

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In agreement with the results of previous MP2 calculations by Sauers, B3LYP, CASSCF, and CASPT2 calculations on the parent 2-carbena-1,3-dioxolane show that it fragments to ethylene plus CO_2 by a concerted pathway with only a small energy barrier. Not only is fragmentation via stepwise C-O bond cleavage computed to be a much higher energy pathway, but the singlet diradical that would be an intermediate along such a reaction path is not even computed to be a local minimum on the potential energy surface.

Key Words : 2-Carbena-1,3-dioxolane, Fragmentation, B3LYP, CASSCF, CASPT2

Introduction

In the formation of olefins from 1,3-dioxolane derivatives such as thionocarbonates (**1a**),[1a] orthoesters (**1b**),[1b] and amide acetals (**1c**),[1c] 2-carbena-1,3-dioxolanes (**2**) have been suggested as plausible intermediates which undergo concerted loss of carbon dioxide (Scheme 1). However, in the pyrolysis of carbonate tosylhydrazone salts (**1d**), some products were formed which indicated that, if carbenadioxolanes are intermediates, they undergo fragmentation by a stepwise process, involving the intermediacy of diradical, (**3**).[2] This conclusion was supported by the finding that, in the pyrolysis of carbonate tosylhydrazones, olefins are formed non-stereospecifically.[3]

The experimental results for carbonate tosylhydrazone salt pyrolyses, suggesting stepwise loss of CO_2 from **2**, were supported by the results of early *ab initio* calculations.[4] These calculations, carried out with the 4-31G basis set, predicted concerted loss of CO_2 from **2** (R=H) to require 30.4 kcal/mol, 8.8 kcal/mol more than a stepwise process involving cleavage of one C-O bond.

However, the absence of polarization functions from the 4-31G basis set and/or inadequate treatment of electron correlation in these early calculations apparently had a

significant effect on the results. Subsequently, when Sauers studied the fragmentation of **2** (R=H) at the MP2/6-31G** level of theory, he found an electronic energy barrier of only 8.8 kcal/mol ($\Delta H_{298} = 6.3$ kcal/mol) for concerted formation of ethylene and carbon dioxide.[5] Unfortunately, MP2 calculations cannot provide a proper description of singlet diradicals; so Sauers did not investigate the stepwise pathway for fragmentation of **2**, involving formation of diradical, **3**.

We have now investigated fragmentation of **2** (R=H) at the CASPT2 level of theory,[6] since CASPT2 calculations should be capable of computing correctly the relative energies of the concerted and stepwise fragmentation of **2**. Herein we report the results of these calculations as well as calculations based on density functional theory (DFT). Both sets of calculations find that the Woodward-Hoffmann allowed, $\sigma^2 s + \sigma^2 s + \omega^2 s$, concerted pathway[7] to be favored over stepwise bond breaking, involving the intermediacy of diradical, **3**. In fact, diradical **3** does not even appear to be a true intermediate on the potential energy surface for **2**.

Computational Methodology

The 6-31G* basis set[8] was used for all the calculations in this study. Calculations based on density functional theory were performed with the three-parameter functional of Becke[9] and the non-local correlation functional of Lee, Yang, and Parr.[10] Geometries were optimized at both the restricted and unrestricted (U)B3LYP level of theories by the standard methods implemented in the *Gaussian 98* suite of programs.[11]

Geometries were also optimized with complete active space (CAS)SCF calculations,[12] which were carried out using both the *Gaussian 98* and *MOLCAS 5.0*[13] suites of programs. The CASSCF calculations were performed with a (10/8) active space. In the (10/8) calculations on **2** the two C-O σ and σ^* orbitals, the two oxygen lone pair π orbitals, and the filled and empty non-bonding AOs on the carbenic carbon were included in the active space, together with the

Scheme 1

1a, X,Y = S
1b, X = OEt, Y = H
1c, X = N̟Me₃, Y = H
1d, X,Y = NNTs

2
Carbenadioxolane

3
Diradical
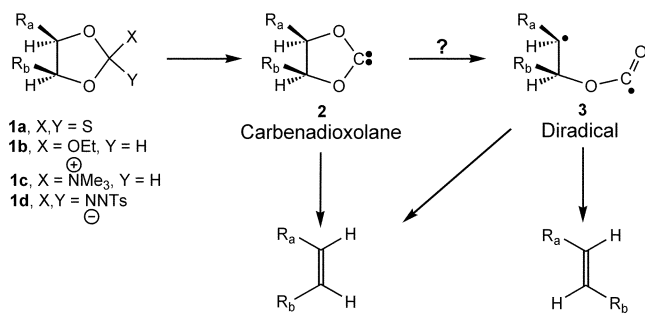
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10 electrons that occupy these 8 orbitals. This active space allows the two equivalent sets of π orbitals in CO_2 to be treated equivalently.

(U)B3LYP, and CASSCF vibrational analyses were carried out for each stationary point, in order to verify its identity as a minimum or a transition state. The vibrational frequencies were used, without scaling, to convert electronic energy differences into enthalpy differences at 298 K.

In order to include the effects of dynamic electron correlation in the CASSCF calculations,[14] CASPT2 single point calculations were carried out at the CASSCF optimized geometries. The CASPT2 calculations were performed with *MOLCAS 5.0.*[13]

Results and Discussion

The B3LYP/6-31G* optimized geometries and energies of singlet carbenadioxolane (**2**, R=H) and the transition structure for its concerted fragmentation to CO_2 and ethylene are given in Table 1. Also given in Table 1 are the geometries and energies of these C_{2v} stationary points that were obtained from the two previous studies of the fragmentation of **2**, R=H.[4,5]

Although the geometries obtained by all three sets of calculations are similar, the relative energies of the reactant and transition structure are not. The B3LYP/6-31G* activation enthalpy at 298 K is computed to be 8.4 kcal/mol, which is 2.1 kcal/mol larger than the value of 6.3 kcal/mol obtained by the MP2/6-31G** calculations, but much smaller than the zero-point corrected, RHF/4-31G electronic energy difference of 30.4 kcal/mol (Table 1).

When we recalculated the RHF activation enthalpy for fragmentation of **2**, R=H with the 6-31G* basis set, a value of 41.2 kcal/mol was obtained. This value is even larger than RHF/4-31G value, showing that the problem with the computational results published in 1981 was not the basis

Table 1. Geometrical parameters,[a] and relative energies and enthalpies of carbenadioxolane (**2**, R=H), the transition structure, and the diradical (**3b**) at the B3LYP/6-31G* level of theory

	R_{C-O}	R_{CH_2-O}	$R_{CH_2-CH_2}$	$\angle$O–C–O	ΔE^b	$\Delta H_{298}{}^b$
Carbena-	1.332	1.478	1.519	109.3	0.0[c]	0.0[d]
dioxolane	*1.33[e]*	*1.47*	*1.51*	*109.0*	*0.0*	*0.0*
(**2**, R=H)	(1.342)[f]	(1.469)	(1.526)	(106.0)	(0.0)	(0.0)
	1.242	1.820	1.428	123.4	10.2	8.4
Transition Structure	*1.26[e]*	*1.72*	*1.44*	*119.4*	*8.8*	*6.3*
	(1.236)[f]	(1.881)	(1.406)	(124.0)	(30.4)	-
Singlet Diradical[g]	1.197	1.471	1.478	130.3	33.6	30.3[h]
(**3b**)	1.319					

[a]Bond lengths, R, in angstroms and bond angles in degrees. [b]Energy and enthalpy differences in kcal/mol. [c]Energies relative to -267.09525 hartrees. [d]Enthalpies relative to -267.02143 hartrees. [e]Values in italics are the MP2/6-31G** results from ref. 5. [f]Values in parentheses are the RHF/4-31G results from ref. 4. [g]Optimized in C_s symmetry at the UB3LYP/6-31G* level. [h]One imaginary frequency excluded from calculation of thermal correction.
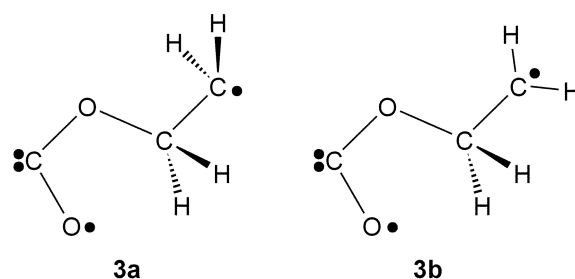
Figure 1. Two conformations of diradical **3**, R=H.

set, but the absence of electron correlation in the calculations.

In order to compare the energies for stepwise and concerted fragmentation of **2**, R=H, the energy of the diradical **3**, R=H, was computed with an unrestricted (U)B3LYP wave function. As in the 1981 study,[4] we carried out calculations on the S-conformation of the heavy atoms,[3] which is shown in Figure 1.

Attempts to optimize the geometry of the singlet diradical in conformation **3a**, in which both singly occupied orbitals lie in the same plane, led to fragmentation to ethylene and CO_2. However, it was possible to optimize a singlet diradical at the geometry of **3b**, in which the singly occupied orbitals lie in orthogonal planes.

The UB3LYP wave function for "singlet" **3b** had $<S^2>$ = 1.01, showing that it is really a 1 : 1 mixture of singlet $<S^2>$ = 0.00 and triplet $<S^2>$ = 2.00 states. At the same geometry the triplet ($<S^2>$ = 2.01) was only 0.1 kcal/mol higher than the UB3LYP "singlet"; so we estimate that the energy of the $<S^2>$ = 0.00 singlet is *ca.* 0.1 kcal/mol below that of the UB3LYP "singlet" with $<S^2>$ = 1.01.

Since the latter is calculated to have an energy 33.6 kcal/mol above that of **2**, R=H, the transition state for concerted fragmentation of the carbenadioxolane is on the order of 20 kcal/mol lower in energy than the singlet diradical. Moreover, a vibrational analysis showed that **3b** has an imaginary frequency for rotating the terminal methylene toward the geometry it has in **3a**. As already noted, **3a** fragments to ethylene plus CO_2 without a barrier. Therefore, not only is singlet diradical **3b** much higher in energy than the transition structure for concerted fragmentation of **2**, R=H, but the singlet diradical does not appear even to be a local energy minimum on the potential energy surface.

Because UB3LYP "singlet" calculations provide highly spin-contaminated wave functions for singlet diradicals, such as **3b**, we also performed calculations on **3b** at the (10/8)CASSCF and (10/8)CASPT2 levels of theory, since these methods are appropriate for dealing with diradicals.[15] Geometries were optimized at the CASSCF level of theory, and single-point energies at these geometries were computed with CASPT2.

The CASPT2 energies, obtained from these calculations on the fragmentation of **2**, R=H, are given in Table 2. The activation enthalpy at 298 K for the concerted fragmentation of **2**, R=H, is 4.0 kcal/mol, which is even smaller than the value of 6.3 kcal/mol, obtained from MP2/6-31G** calculations by Sauers.[5] The energy difference between **2**,

Table 2. Geometrical parameters[a], and relative energies and enthalpies of carbenadioxolane (**2**, R=H), the transition structure, and the diradical (**3b**) at the (10/8)CASPT2/6-31G*//(10/8) CASSCF/6-31G* level of theory

	R_{C-O}	R_{CH_2-O}	$R_{CH_2-CH_2}$	$\angle$O–C–O	ΔE^b	$\Delta H_{298}{}^b$
Carbena-dioxolane (**2**, R=H)	1.313	1.459	1.517	108.8	0.0	0.0
Transition Structure	1.235	1.807	1.428	122.1	6.2	4.0
Singlet Diradical (**3b**)	1.183 1.302	1.474	1.486	130.2	29.2	25.2^d

[a]Bond lengths, R, in angstroms and bond angles in degrees. [b]Energies relative to -266.32458 hartrees. [c]Enthalpies relative to -266.24648 hartrees. [d]Two imaginary frequencies excluded from calculation of thermal correction.

R=H, and the singlet diradical **3b** is computed to be 29.2 kcal/mol. Therefore, at the CASPT2 level, the energy difference between the concerted and stepwise pathways for fragmentation of **2**, R=H, is 23.0 kcal/mol, which is just 0.4 kcal/mol smaller than the (U)B3LYP energy difference between these two pathways.

Finally, as was the case at the B3LYP level, a (10/8)CASSCF vibrational analysis found that **3b** has two imaginary frequencies corresponding to the two possible out-of-plane motions of the hydrogens on the terminal methylene. These motions shift the geometry of the diradical from **3b** toward the geometry it has in **3a**, which at the CASSCF level, also undergoes fragmentation to ethylene plus CO_2 without a barrier. Therefore, both the B3LYP and CASSCF calculations indicate that singlet diradical **3** does not exist as even a local energy minimum on the potential energy surface.

Conclusions

In agreement with the MP2 results of Sauers,[5] our B3LYP, CASSCF, and CASPT2 calculations on **2**, R=H, indicate that carbenadixolanes fragment by concerted loss of CO_2 with only a small energy barrier. Not only is fragmentation via stepwise C-O bond cleavage computed to be a much higher energy pathway, but also singlet diradical **3** is not even computed to be a true intermediate on the potential energy surface for fragmentation of **2**, R=H.

The products formed from pyrolysis of carbonate tosylhydrazone salts are clearly formed by a pathway that does not involve concerted cleavage of both C-O bonds.[2,3]

Therefore, our calculations lead us to conclude that singlet carbendioxolanes (**2**) are not formed as intermediates in these pyrolyses.

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