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Singlet−Triplet Splittings and Barriers to Wolff Rearrangement for Carbonyl Carbenes

Anthony P. Scott, Matthew S. Platz, and Leo Radom*

*Contribution from the Research School of Chemistry, Australian National University,
Canberra, ACT 0200, Australia, and Department of Chemistry, Ohio State University,
Columbus, Ohio 43210*

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Abstract: High-level ab initio calculations at the G3(MP2)//B3-LYP level have been used to study carbomethoxychlorocarbene and related halogenocarbenes and carbonyl carbenes. Initial calculations at the more accurate W1′ level on the subset CH_2, HCCl, HCF, CCl_2, and CF_2 provide support for the reliability of G3(MP2)//B3-LYP for this type of problem. The W1′ calculations also suggest that the experimental S−T splitting is slightly underestimated for HCCl and CF_2 and substantially underestimated for CCl_2, in keeping with other recent high-level studies. Whereas the parent carbonyl carbenes, namely formylcarbene, carbohydroxycarbene, and carbomethoxycarbene, are all predicted to have triplet ground states, their chloro and fluoro derivatives are predicted to have singlet ground states. In particular, carbomethoxychlorocarbene is predicted to have a singlet ground state, with the singlet−triplet splitting estimated as -16.0 kJ mol^{-1}. The barriers to Wolff rearrangement of the singlet carbonyl carbenes generally (but not always) correlate with the exothermicity accompanying the production of ketenes. In the case of the parent carbonyl carbenes, for which the rearrangement reaction is most exothermic, the barriers lie between about 10 and 30 kJ mol^{-1}, whereas for the less exothermic rearrangements of the chloro- and fluoro-substituted carbonyl carbenes, the Wolff rearrangement barriers increase significantly to between 58 and 75 kJ mol^{-1}. The calculated barrier for carbomethoxychlorocarbene is 58.2 kJ mol^{-1}.

Introduction

Carbenes are important intermediates in a variety of chemical reactions and have therefore been extensively studied both experimentally and theoretically.[1] Carbenes have low-lying singlet and triplet states and, because their reactivity is state-specific, the magnitude of the singlet−triplet (S−T) splitting is of great importance and has received particular attention.[2,3] Carbonyl carbenes (YC−CO−X) are widely used in synthesis[4] and in industry as photoresists.[5] A key reaction that singlet carbonyl carbenes can undergo is the Wolff rearrangement,[6] leading to the production of a ketene:

In an accompanying paper, Platz and co-workers[7] describe the generation and experimental characterization of carbomethoxychlorocarbene (ClC−CO−OCH_3, **4-Cl**). One of the attractive features of carbomethoxychlorocarbene is that it is believed to be a ground-state singlet, unlike its parent formylcarbene (HC−CO−H, **2-H**) which is a ground-state triplet. This means that experimental study of the Wolff rearrangement, which takes place on the singlet surface, is no longer complicated by the surface crossing that is required for carbenes such as formylcarbene that have a triplet ground state.

Platz and co-workers[7] were able to produce **4-Cl** as a persistent species in argon at 14 K and as a transient species in the solution phase, and to examine its spectroscopic properties and reaction kinetics. Theoretical calculations at a fairly simple level (B3-LYP/6-31G(d)) were used to help with the characterization through predictions of infrared and ultraviolet spectra. The matrix isolation UV−vis and IR spectra of **4-Cl** were found to be more consistent with the spectra predicted for the singlet state rather than the triplet of this carbene.[7] However, because the B3-LYP/6-31G(d) procedure actually predicts a triplet

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ground state for **4-Cl**, it is desirable to examine carbomethoxychlorocarbene using higher level calculations to obtain definitive evidence that the ground state is indeed a singlet and to obtain more reliable estimates of the singlet−triplet splitting. In the experimental study, the lifetime of **4-Cl** was measured in solution along with the barrier to the disappearance of the carbene.[7] However, the kinetic analysis does not reveal whether carbene **4-Cl** is consumed by Wolff rearrangement under the experimental conditions or by a mix of intra- and intermolecular processes. Higher level calculations of the Wolff rearrangement barrier of **4-Cl** are thus urgently needed to help interpret the experimentally determined barrier to carbene decay.

The singlet−triplet splitting in carbenes has attracted considerable previous experimental and theoretical attention. In particular, there have been a number of recent detailed theoretical studies of the S−T splitting in halogenocarbenes[8−17] but the carbonyl carbenes have been less studied.[18,19] Detailed theoretical examinations of the Wolff rearrangement in the simplest carbonyl carbene, formylcarbene, were reported some 20 years ago,[20,21] while an updated treatment has been presented more recently.[22]

The primary goals of the present work are to use high-level theoretical procedures to determine the singlet−triplet splitting in carbomethoxychlorocarbene (**4-Cl**) and its barrier to Wolff rearrangement, and to obtain comparative data for related carbonyl carbenes. To accomplish this, a number of ab initio procedures are initially used to examine prototype systems for which either reliable experimental data are available or we can carry out high-level calculations. These results, which are also of interest in their own right, are used to establish confidence levels for the predictions of the theoretical procedures that we apply to **4-Cl** and related carbenes.

Theoretical Procedures

Ab initio molecular orbital theory[23] and density functional theory[24] calculations were carried out using the Gaussian 94,[25a] Gaussian 98,[25b] and Molpro 2000[26] programs. Levels of theory examined range from gradient-corrected B-LYP and hybrid B3-LYP density functional theory calculations with the 6-31G(d) and 6-311+G(3df,2p) basis sets to high-level composite procedures including G3(MP2)//B3-LYP[27] and W1′.[28] For all the density functional theory calculations, zero-point vibrational energy (ZPVE) corrections, required to correct the raw relative energies to 0 K, were obtained from B3-LYP/6-31G(d) harmonic vibrational frequencies scaled by 0.9806.[29]

The density functional theory procedures (B-LYP and B3-LYP) are potentially applicable to large systems, G3(MP2)//B3-LYP is more reliable but restricted to medium-sized systems, while W1′ is a high-accuracy procedure but very demanding of computational resources and therefore currently restricted to small systems. More specifically, G3(MP2)//B3-LYP[27] corresponds effectively to QCISD(T)(fc) calculations with the G3MP2large basis set (assuming additivity of basis set and correlation effects) on B3-LYP/6-31G(d) optimized structures with standard spin−orbit, zero-point vibrational energy (calculated from B3-LYP/6-31G(d) vibrational frequencies scaled by 0.96) and higher level corrections. This method has been found[27] to predict relative energies for a large test set with a mean absolute deviation from reliable experimental values of 5.2 kJ mol^{-1}. The W1′ procedure attempts to extrapolate to infinite-basis-set CCSD(T) calculations, and includes core-correlation, scalar-relativistic, and spin−orbit contributions, using geometries optimized at the B3-LYP/cc-pVTZ+1 level and ZPVEs calculated from B3-LYP/cc-pVTZ+1 frequencies scaled by 0.985. It has been found[28] to produce relative energies for a smaller test set with a mean absolute deviation from experiment of 1.3 kJ mol^{-1}. W1′ is the highest level of theory used in the present study.

Initial calculations were carried out for the singlet−triplet separations in the prototype carbenes, CH_2, HCCl, HCF, CCl_2, and CF_2, for which direct experimental data are available,[3a,30−32] and for HC−CO−H as a representative of the carbonyl carbenes. These were carried out at all the levels of theory, including W1′.

For the Wolff rearrangement, formylcarbene (HC−CO−H) was used as the test system on which to apply the full range of calculations. This system has been previously examined in detail with high-level calculations,[22] and the previous work has been supplemented here by additional calculations including W1′.

On the basis of these detailed calculations on a limited set of molecules, the G3(MP2)//B3-LYP method was selected for uniform application to the full set of molecules, allowing changes with substitution pattern to be analyzed. Stabilization energies for carbenes and ketenes were obtained as energy changes for the reactions

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$$\mathrm{YCW} + 2\mathrm{CH_4} \rightarrow \mathrm{CH_2} + \mathrm{CH_3Y} + \mathrm{CH_3W} \quad (1)$$

$$\mathrm{YC{-}CO{-}X} + 2\mathrm{CH_4} \rightarrow \mathrm{HC{-}CO{-}H} + \mathrm{CH_3X} + \mathrm{CH_3Y} \quad (2)$$

and

$$\mathrm{XYC{=}C{=}O} + 2\mathrm{CH_4} \rightarrow \mathrm{H_2C{=}C{=}O} + \mathrm{CH_3X} + \mathrm{CH_3Y} \quad (3)$$

Finally, the effect of solvent was estimated in a small number of cases using the self-consistent isodensity polarizable continuum model (SCIPCM),[33] as implemented in Gaussian 94.[25a] In this model, the solute is taken to occupy a cavity that is determined self-consistently from an isodensity surface (0.0004 au), and the solvent is represented by a continuous dielectric, characterized by a given dielectric constant (ϵ). The calculations were carried out at the B3-LYP/6-311+G(3df,2p) level without re-optimization of the solvated structures and for dielectric constants of 2 (representing a nonpolar solvent) and 40 (representing a polar solvent).[34]

Unless otherwise noted, relative energies within the text refer to G3-(MP2)//B3-LYP values at 0 K, since these are available for all the molecules examined in the present study. Results at this level are conservatively considered to be accurate to ±8 kJ mol^{-1}. Selected relative energies and structural data are presented in the tables and figures within the text. Calculated total energies are included in Table S1 of the Supporting Information, while Gaussian archive entries for the optimized structures are collected in Table S2.

Results and Discussion

Singlet−Triplet Splittings in Prototype Carbenes. Singlet−triplet splittings, calculated at a number of levels of theory for prototype carbenes, are presented in Table 1. The carbenes include CH_2, (**1-H**), HCCl (**1-Cl**), HCF (**1-F**), CCl_2 (**1-Cl$_2$**), and CF_2 (**1-F$_2$**), for which experimental data are available,[3a,30−32] and HC−CO−H, which is representative of the carbonyl carbenes that form the main focus of this paper. A positive S−T value implies that the singlet lies higher in energy than the triplet.

The W1′ procedure gives close agreement with experiment (to within 1 kJ mol^{-1}) for CH_2 and HCF for which very reliable experimental information (as indicated by the error bars of less than 2 kJ mol^{-1})[31,32] is available (Table 1). This lends confidence to the use of W1′ values to assess other theoretical and experimental singlet−triplet splittings. In this respect, although the W1′ value for HCCl (−24.8 kJ mol^{-1}) lies within the experimental error bars (−17.6 ± 10.5 kJ mol^{-1}),[32] it suggests that the experimental estimate of the singlet−triplet splitting is a slight underestimate. This is in agreement with results of other recent high-level theoretical studies.[9,12,13,16] Likewise, our W1′ S−T splitting for CF_2 (−236.6 kJ mol^{-1}) lies within the error bars of a recent experimental estimate (−225.9 ± 12.6 kJ mol^{-1})[3a] but our W1′ result and other recent high-level theoretical values[9,12,13,15,16] suggest that this experimental splitting is also underestimated. An older experimental value (−236.8 kJ mol^{-1})[30] is closer to the best theoretical results. For CCl_2, the discrepancy between the W1′ (−83.4 kJ mol^{-1}) and experimental (−12.6 ± 12.6 kJ mol^{-1})[3a] estimates is very large and well beyond the experimental error bars. This again is in keeping with other recent high-level studies[9,12.13,16,17] and suggests, as pointed out by Barden and Schaefer,[17] that a re-interpretation of the experimental data[3a] would be desirable. For HC−CO−H, where there is no experimental value of the singlet−triplet splitting available, we use the W1′ value (15.0 kJ mol^{-1}) as the reference for the evaluation of the other procedures described below.

B3-LYP consistently favors the triplet state of the carbenes relative to the singlet, i.e., S−T is too positive or not sufficiently negative (Table 1). With B3-LYP/6-311+G(3df,2p), the errors (compared with W1′) in the singlet−triplet splitting lie in the range +6.6 to +17.2 kJ mol^{-1}. B-LYP performs better than B3-LYP in an absolute sense, as found in previous work,[13,14] but the error is less systematic, e.g. the triplet is no longer always preferentially favored. The errors for B-LYP/6-311+G(3df,2p) lie in the range −11.7 to +10.8 kJ mol^{-1}.

Finally, G3(MP2)//B3-LYP gives singlet−triplet splittings reasonably close to the W1′ results. The errors range from −6.5 to +2.2 kJ mol^{-1}, with a mean absolute deviation of 3.3 kJ mol^{-1}. We have therefore selected the G3(MP2)//B3-LYP procedure to examine the singlet−triplet splittings in the larger carbenes in this study (for which W1′ is inaccessible in some cases).

Geometries of Carbonyl Carbenes. The B3-LYP/6-31G(d) optimized structures of the carbonyl carbenes (YC−CO−X) are included in Table S2 of the Supporting Information as Gaussian archive files. We present here only some of the highlights, focusing primarily on our main target molecule, carbomethoxychlorocarbene (**4-Cl**). Selected structural parameters are presented in Table 2.

The triplet carbenes all have C_s symmetry and a syn orientation of the C−Y bond with respect to C═O, as reflected in ∠YCCO dihedral angles of 0.0°. In contrast, the singlet carbenes all have a near-orthogonal orientation about the C−C bond, as reflected in ∠YCCO dihedral angles of 80.4−93.3°. A notable feature in singlet **2-H**, **3-H**, and **4-H** is the narrow ∠CCO bond angle (96−104°), reflecting a favorable interaction between the carbonyl oxygen and the formally vacant p orbital at the carbene center, as discussed further below. For both the carbohydroxy (X = OH) and carbomethoxy (X = OMe) systems, the preferred conformations have a syn (triplet) or near-syn (singlet) orientation of the O−Z bond (Z = H or Me) with respect to C═O.

Optimized B3-LYP geometries of the best singlet and triplet structures of carbomethoxychlorocarbene (**4-Cl**) are presented in Figure 1. These represent specific examples of the general structural features noted above. In particular, singlet **4-Cl** shows a ∠ClCC═O dihedral angle of 93.3° and an ∠OCOMe dihedral angle of 1.4°. The geometrical parameters calculated with the 6-31G(d) and 6-311+G(3df,2p) basis sets are very similar, and the differences between them are generally systematic. For example, the bond lengths generally shorten slightly on going to the larger basis set. This provides some justification for the use of B3-LYP/6-31G(d) geometries in the G3(MP2)//B3-LYP procedure.

Singlet−Triplet Splittings in Carbonyl Carbenes. A comparison of singlet−triplet splittings for carbonyl carbenes and related parent systems, calculated at the G3(MP2)//B3-LYP level, is presented in Figure 2.

It is well-known that the parent carbene, methylene (**1-H**), has a triplet ground state.[2,31] We can see from the data in Table 3 and Figure 2 that the singlet is strongly stabilized by chloro substitution and even more so by fluoro substitution, while the effect on the triplet is much smaller, to the extent that HCCl (**1-Cl**) and HCF (**1-F**) have singlet ground states. This effect, which has previously been discussed in detail,[8,10] may be rationalized by noting that simple singlet carbenes are π-elec-

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(34) Re-optimization of the solvated structures leads to minimal changes in relative energies compared with single-point SCIPCM calculations on the gas-phase structures. For example, the singlet−triplet splitting in solvated formylcarbene changes by less than 0.1 kJ mol^{-1} on re-optimizing the solvated structure.

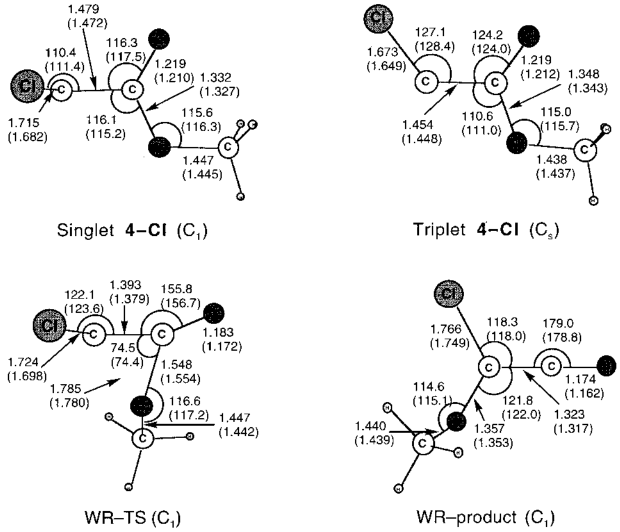
Table 1. Calculated Singlet−Triplet Splittings for Prototype Systems (0 K, kJ mol^{-1})[a]

level[b]	CH_2 **1-H**	HCCl **1-Cl**	HCF **1-F**	CCl_2 **1-Cl$_2$**	CF_2 **1-F$_2$**	HCCHO **2-H**
B3-LYP/6-31G(d)	55.0	−10.2	−51.4	−70.5	−218.0	32.7
B3-LYP/6-311+G(3df,2p)	45.0	−16.0	−49.7	−72.8	−219.4	24.5
B-LYP/6-31G(d)	48.8	−22.2	−58.8	−90.3	−225.2	9.9
B-LYP/6-311+G(3df,2p)	39.8	−25.5	−56.2	−88.0	−225.8	3.3
G3(MP2)//B3-LYP[c]	39.5	−28.3	−60.6	−89.9	−234.4	10.0
W1′ [d]	38.4	−24.8	−61.4	−83.4	−236.6	15.0
expt	37.65 ± 0.06[e]	−17.6 ± 10.5[f]	−62.3 ± 1.7[f]	−12.6 ± 12.6[g]	−225.9 ± 12.6[g] −236.8[h]	

[a] A positive value signifies a triplet ground state. Theoretical values include (scaled by 0.9806) B3-LYP/6-31G(d) ZPVEs, unless otherwise noted. [b] Optimized at the theoretical level noted unless otherwise noted. [c] Optimized at B3-LYP/6-31G(d). ZPVE calculated at B3-LYP/6-31G(d) scaled by 0.96. [d] Optimized at B3-LYP/cc-pVTZ+1. ZPVE calculated at B3-LYP/cc-pVTZ+1, scaled by 0.985. [e] From ref 31. [f] From ref 32. [g] From ref 3a. [h] From ref 30.

Table 2. Selected Geometrical Parameters (B3-LYP/6-31G(d)) for Carbonyl Carbenes (YC−CO−X) and for the Transition Structures for the Wolff Rearrangement (WR)

				triplet carbene			singlet carbene			WR TS	
		Y	X	∠YCCO	∠CCO	∠CCX	∠YCCO	∠CCO	∠CCX	∠CCO	∠CCX
HC−CO−X	**2-H**	H	H	0.0	119.6	118.8	80.4	96.1	136.7	125.7	110.7
	3-H	H	OH	0.0	122.1	114.5	83.2	103.8	129.0	135.6	97.8
	4-H	H	OMe	0.0	121.9	113.7	83.5	102.1	129.8	132.3	100.6
ClC−CO−X	**2-Cl**	Cl	H	0.0	122.5	114.9	84.1	118.1	117.3	148.1	86.5
	3-Cl	Cl	OH	0.0	124.4	111.3	92.2	117.0	116.3	155.1	76.5
	4-Cl	Cl	OMe	0.0	124.2	110.6	93.3	116.3	116.1	155.8	74.5
FC−CO−X	**2-F**	F	H	0.0	121.2	115.0	81.2	116.2	119.0	151.3	78.7
	3-F	F	OH	0.0	123.7	111.3	89.0	117.2	116.0	156.4	72.8
	4-F	F	OMe	0.0	123.5	110.6	89.8	116.7	115.7	156.4	71.0



Singlet **4-Cl** (C_1) Triplet **4-Cl** (C_s)

WR−TS (C_1) WR−product (C_1)

Figure 1. Selected structural parameters for B3-LYP/6-31G(d) and B3-LYP/6-311+G(3df,2p) (in parentheses) optimized structures of singlet and triplet carbomethoxychlorocarbene (**4-Cl**), and the transition structure and product of the Wolff rearrangement (WR).

tron-deficient and σ-electron-rich and so they are effectively stabilized by π-electron-donor, σ-electron-acceptor substituents such as Cl or F. Note that fluoro substitution has a greater effect than chloro substitution for the singlet whereas for the triplet the reverse applies. The latter result is consistent with the greater stabilizing effect at a radical center of chloro substitution compared with fluoro substitution.[35,36]

The formyl substituent is normally a π-electron acceptor and therefore might not be expected to significantly stabilize a singlet carbene in a hypothetical planar structure. However, a rotation about the C−C bond of roughly 90° in singlet formylcarbene (**2-H**) leads to the possibility of donation by the in-plane oxygen lone pair of the carbonyl group to the formally vacant p orbital of the carbene. The occurrence of such an interaction is reflected in the near-orthogonal calculated ∠HCCO dihedral angle of 80.4°, as noted above, and the narrow ∠CCO bond angle of 96.1° (Table 2). In addition, donation by the sp^2-type lone pair of the carbene to the π* orbital of the C═O double bond is now possible. These interactions lead to preferential stabilization (relative to CH_2) of the singlet (Table 3) and a significant reduction in the S−T gap (Figure 2). However, the triplet is still calculated to be favored by 10.0 kJ mol^{-1} with G3(MP2)//B3-LYP. This is reasonably close to the W1′ estimate of 15.0 kJ mol^{-1} for the S−T gap. Our SCIPCM solvation calculations indicate that solvation preferentially stabilizes singlet **2-H** over triplet **2-H** by 2 ($\epsilon = 2$) to 6 ($\epsilon = 40$) kJ mol^{-1}. The resultant

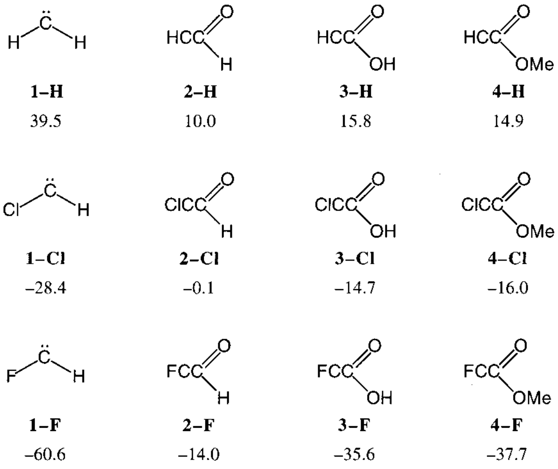


Figure 2. Diagrammatic comparison of singlet−triplet splittings (G3-(MP2)//B3-LYP, 0 K, kJ mol^{-1}).

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(35) The calculated stabilization energies at a radical center due to F and Cl substituents are 13.9 and 23.0 kJ mol^{-1}, respectively (CBS-RAD level).[36]

(36) Henry, D. J.; Parkinson, C. J.; Mayer, P. M.; Radom, L. *J. Phys. Chem. A.* In press.

Table 3. Calculated Stabilization Energies (G3(MP2)//B3-LYP, 0 K, kJ Mol^{-1}) for Carbenes[a,b] and Ketenes[c]

species	singlet	triplet
HCH (**1-H**)[a]	0.0	0.0
HCCl (**1-Cl**)[a]	100.6	32.8
HCF (**1-F**)[a]	118.2	18.1
ClCCl (**1-Cl$_2$**)[a]	186.4	56.9
FCF (**1-F$_2$**)[a]	296.7	22.8
HC−CO−H (**2-H**)[a]	66.7	37.2
HC−CO−OH (**3-H**)[a]	44.7	20.9
HC−CO−OMe (**4-H**)[a]	46.7	22.1
ClC−CO−H (**2-Cl**)[a]	120.2	80.6
ClC−CO−OH (**3-Cl**)[a]	113.6	59.3
ClC−CO−OMe (**4-Cl**)[a]	117.3	61.8
FC−CO−H (**2-F**)[a]	123.2	69.7
FC−CO−OH (**3-F**)[a]	120.3	45.2
FC−CO−OMe (**4-F**)[a]	124.8	47.5
HC−CO−H (**2-H**)[b]	0.0	
HC−CO−OH (**3-H**)[b]	115.5	
HC−CO−OMe (**4-H**)[b]	116.5	
ClC−CO−H (**2-Cl**)[b]	53.4	
ClC−CO−OH (**3-Cl**)[b]	184.5	
ClC−CO−OMe (**4-Cl**)[b]	187.1	
FC−CO−H (**2-F**)[b]	56.5	
FC−CO−OH (**3-F**)[b]	191.2	
FC−CO−OMe (**4-F**)[b]	194.6	
$H_2C{=}C{=}O$[c]	0.0	
$H(OH)C{=}C{=}O$[c]	−23.5	
$H(OMe)C{=}C{=}O$[c]	−25.5	
$ClHC{=}C{=}O$[c]	−24.3	
$Cl(OH)C{=}C{=}O$[c]	−18.0	
$Cl(OMe)C{=}C{=}O$[c]	−15.3	
$FHC{=}C{=}O$[c]	−50.2	
$F(OH)C{=}C{=}O$[c]	−22.8	
$F(OMe)C{=}C{=}O$[c]	−22.4	

[a] Energies of formal reactions 1: $YCW + 2CH_4 \rightarrow CH_2 + CH_3Y + CH_3W$. [b] Energies of formal reactions 2: $YC{-}CO{-}X + 2CH_4 \rightarrow HC{-}CO{-}H + CH_3X + CH_3Y$. [c] Energies of formal reactions 3: $XYCCO + 2CH_4 \rightarrow H_2CCO + CH_3X + CH_3Y$.

small singlet−triplet separation calculated for **2-H** (e.g. 9 kJ mol^{-1} for $\epsilon = 40$ with W1′) is consistent with laser flash photolysis studies which demonstrate that the singlet state of formylcarbene is easily accessible to the spin-equilibrated carbene sample at ambient temperature.[37]

The singlet-stabilizing effect of carbonyl substitution is slightly moderated in the carbohydroxy- (**3-H**) and carbomethoxy- (**4-H**) carbenes, relative to formylcarbene, leading to S−T splittings of 15.8 and 14.9 kJ mol^{-1}, respectively. This change can be attributed in part to a decreased interaction between the sp^2-type carbene lone pair and the π^* C=O orbital of the acid (**3-H**) or ester (**4-H**) systems, since these orbitals lie higher in energy than the π^* C=O orbital of **2-H** (and are therefore poorer acceptors).[38]

The triplets are also less stabilized (Table 3), which may be attributed to the reduced radical-stabilizing influence of the carboxylic acid and ester groups relative to the formyl group.[36,39] The overall result is a decreased relative stabilization of the singlet in **3-H** and **4-H** compared with **2-H**. Laser flash photolysis studies of carboethoxycarbene,[40] which is of course closely related to **4-H**, indicate that the singlet and triplet states of this carbene readily interconvert in solution at ambient temperature and therefore must be rather close in energy, consistent with the results of the present gas-phase calculations.

In a previous high-level study of the S−T splitting in carbohydroxycarbene, Xie and Schaefer[19] estimated a value of 19.7 kJ mol^{-1} on the basis of calculations at the CCSD(T)/TZ2Pf//CISD/TZ2P level, which is close to our calculated S−T value for **3-H**. The slight difference may be associated with the use of the CISD/TZ2P value of 116.3° for the ∠CCO angle. Intriguingly, the ∠CCO angle in singlet **3-H** is sensitively dependent on the theoretical procedure used. For example, while CISD/6-31G(d) gives 116.0°, B3-LYP/6-31G(d) gives 103.8°, and the higher level CCSD(T)/6-31G(d) procedure predicts a ∠CCO angle of 102.9°. Previous calculations have shown that the ∠CCO angle in formylcarbene is also very sensitive to the level of theory used, with B3-LYP again producing results close to those of CCSD(T).[22]

We note from Table 2 that the ∠CCO bond angles in **3-H** and **4-H** are significantly larger than that of **2-H**. This result may reflect the relative stabilities of the related oxirenes. In the case of **2-H**, the oxirene isomer lies only slightly higher in energy than the carbene.[22,41] In contrast, hydroxyoxirene is strongly destabilized with respect to its carbene isomer **3-H**. As a consequence, the tendency for a bridging-type structure is reduced and the ∠CCO angles are widened.

Because chloro substitution decreases the extent to which the carbene center is π-electron deficient, singlet formylchlorocarbene (**2-Cl**) appears not to benefit from the donation by the in-plane oxygen lone pair of the carbonyl group to the formally vacant p orbital of the carbene.[42] This is reflected in a widened bond angle of 118.1° compared with 96.1° in **2-H**, and in a stabilization energy for singlet ClC−CO−H (120.2 kJ mol^{-1}, Table 3) that is significantly less than the sum of the stabilization effects of individual chloro and formyl substituents at a carbene center (167.3 kJ mol^{-1}). However, the donation by the sp^2-type lone pair of the carbene to the π^* orbital of the C=O double bond is still favorable and the ∠ClCCO dihedral angle is therefore still close to orthogonal (84.1°).

The S−T separation in **2-Cl** is −0.1 kJ mol^{-1}, which means that chloro substitution in **2-H** has relatively stabilized the singlet but formyl substitution in **1-Cl** has relatively stabilized the triplet, as is also clear from the data in Table 3. The latter result can be rationalized in terms of interaction of the formally singly occupied p orbital at the carbene center of triplet **2-Cl** with the π^* C=O orbital, analogous to the corresponding stabilizing interaction of a carbonyl group at a radical center.[36,39,43] The triplet is relatively less stabilized in carbohydroxychlorocarbene (**3-Cl**) and carbomethoxychlorocarbene (**4-Cl**). As before, this may be attributed to the reduced radical-stabilizing influence of the carboxylic acid and ester groups relative to the formyl group,[36,39] an effect that would be expected to carry over to the triplet carbenes. The reduction in the carbonyl group stabilization of singlet **2-Cl** by the OH and OMe substituents is less than it

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(37) Toscano, J. P.; Platz, M. S.; Nikolaev, V. *J. Am. Chem. Soc.* **1995**, *117*, 4712−4713.

(38) This type of effect can also explain inter alia the higher acidity of the α C−H bonds of ketones compared with the corresponding C−H bonds of esters.

(39) The calculated stabilization energy at a radical center due to a CHO group is 40.0 kJ mol^{-1}, compared with 24.6 and 25.1 kJ mol^{-1} for COOH and COOMe, respectively (CBS-RAD level).[36]

(40) Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popic, V. *J. Am. Chem. Soc.* **1994**, *116*, 8146−8151.

(41) We have carried out G3(MP2)//B3-LYP calculations (without ZPVE) on oxirenes in which the two C−O bonds of the oxirene ring are constrained to be equal. Without this constraint, the oxirene generally collapses to alternative isomers. At this level, the oxirene structure is calculated to lie 5.1 kJ mol^{-1} above **2-H** but the energy difference jumps to 78.7 kJ mol^{-1} for hydroxyoxirene when compared with **3-H**.

(42) In addition, constrained[41] calculations at the G3(MP2)//B3-LYP level indicate that chloro- and fluorooxirene lie 49.2 and 67.7 kJ mol^{-1}, respectively, higher in energy than the corresponding carbenes **2-Cl** and **2-F**.

(43) Bernard, F.; Epiotis, N. D.; Cherry, W.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 469−478.

Table 4. Calculated Barriers and Exothermicities for the Wolff Rearrangement for Formylcarbene (**2-H**) (0 K, kJ mol^{-1})[a]

level[b]	barrier	exothermicity
B3-LYP/6-31G(d)	15.7	−322.3
B3-LYP/6-311+G(3df,2p)	11.4	−327.0
B-LYP/6-31G(d)	32.2	−302.0
B-LYP/6-311+G(3df,2p)	26.5	−307.9
G3(MP2)//B3-LYP[c]	24.9	−316.3
W1′ [d]	18.5	−323.4
CCSD(T)//CCSD(T)[e]	20.6	−327.5

[a] Theoretical values include (scaled by 0.9806) B3-LYP/6-31G(d) ZPVEs, unless otherwise noted. [b] Optimized at the specified theoretical level unless otherwise noted. [c] Optimized at B3-LYP/6-31G(d). ZPVE calculated at B3-LYP/6-31G(d) scaled by 0.96. [d] Optimized at B3-LYP/cc-pVTZ+1. ZPVE calculated at B3-LYP/cc-pVTZ+1, scaled by 0.985. [e] Best estimate from ref 22. Corresponds to large-basis-set CCSD(T) calculation.

is in **2-H**, because electronegative substitution makes the sp^2-type lone pair in **2-Cl** a poorer donor in the first place. This is reflected in singlet stabilization energies for **3-Cl** and **4-Cl** that are quite close to that of **2-Cl** (Table 3). For our main target system, carbomethoxychlorocarbene (**4-Cl**), the singlet is indeed the ground state, and it is favored over the triplet by 16.0 kJ mol^{-1}.

Results for the fluoro-substituted carbenes (**1-F**, **2-F**, **3-F**, **4-F**) are qualitatively the same as for the chloro-substituted systems. However, because of the increased singlet-stabilizing effect and reduced triplet-stabilizing effect of the fluoro substituent, the S−T separations are considerably more negative than for the corresponding chloro systems. For example, carbomethoxyfluorocarbene (**4-F**) is predicted to have a ground-state singlet lying 37.7 kJ mol^{-1} below the triplet.

In summary, the singlet−triplet ordering in methylene is reversed with chloro and fluoro substitution because of the strong singlet-stabilizing effects of these substituents. The formyl, carbohydroxy, and carbomethoxy substituents all relatively stabilize the singlet in methylene (first row of Figure 2) but relatively stabilize the triplet in chlorocarbene and fluorocarbene (second and third rows of Figure 2) where singlet influences are reduced and triplet influences enhanced. It is important to note that the effects of substituents are not simply additive, so that it is difficult to make intuitive estimates. Finally, the carbohydroxy and carbomethoxy substituents show very similar behavior. The target system, carbomethoxychlorocarbene (**4-Cl**), has a ground-state singlet that lies 16 kJ mol^{-1} below the triplet. As noted above, this result is estimated to be accurate to within ±8 kJ mol^{-1}.

Wolff Rearrangement Barrier and Exothermicity in Formylcarbene. A detailed high-level theoretical study of the Wolff rearrangement in formylcarbene has been reported by Scott et al.[22] We supplement the previous results here by including barriers and exothermicities calculated with the levels of theory that are of interest in the present study. These are presented in Table 4.

Our best value (W1′) for the barrier is 18.5 kJ mol^{-1}. This is quite close to the large-basis-set CCSD(T) estimate (20.6 kJ mol^{-1}) obtained previously.[22] B3-LYP/6-311+G(3df,2p) gives a barrier (11.4 kJ mol^{-1}) that is somewhat too low while B-LYP/6-311+G(3df,2p) gives a barrier (26.5 kJ mol^{-1}) that is correspondingly too high. The G3(MP2)//B3-LYP value (24.9 kJ mol^{-1}) is also slightly too high.

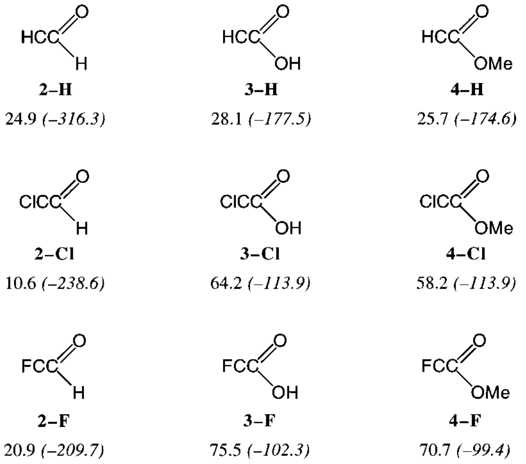

Figure 3. Diagrammatic comparison of barriers (normal type) and exothermicities (in italics and parentheses) for Wolff rearrangement reactions of carbonyl carbenes (G3(MP2)//B3-LYP, 0 K, kJ mol^{-1}).

The W1′ value for the exothermicity is −323.4 kJ mol^{-1}. This is again quite close to the large-basis-set CCSD(T) estimate (−327.5 kJ mol^{-1}) obtained previously,[22] and to the B3-LYP/6-311+G(3df,2p) value (−327.0 kJ mol^{-1}). The B-LYP/6-311+G(3df,2p) result (−307.9 kJ mol^{-1}) is in less good agreement. G3(MP2)//B3-LYP (−316.3 kJ mol^{-1}) slightly underestimates the exothermicity.

Wolff Rearrangement Barriers and Exothermicities for Carbonyl Carbenes. Barriers and reaction exothermicities for the Wolff rearrangement of carbonyl carbenes, as calculated with G3(MP2)//B3-LYP, are displayed in Figure 3.

Our starting point is formylcarbene (**2-H**) for which the calculated G3(MP2)//B3-LYP Wolff rearrangement barrier is 24.9 kJ mol^{-1} and the exothermicity is −316.3 kJ mol^{-1}. The transition structure is relatively early, as reflected in the ∠CCO angle of 125.7° (which becomes 180.0° in ketene) and the ∠CCH angle of 110.7° (which becomes 26.9° in ketene) (see Table 2).

The exothermicity of the formylcarbene-to-ketene rearrangement (−316.3 kJ mol^{-1}) is reduced substantially for all the substituents that we have examined. The results may be rationalized by examining the calculated stabilization energies of the carbonyl carbenes (eq 2) and ketenes (eq 3) in Table 3. Ketene is destabilized to a modest degree (−15.3 to −50.2 kJ mol^{-1}) by all the substituents while formylcarbene is always stabilized, sometimes by a substantial amount (53.4 to 194.6 kJ mol^{-1}). The combination of these two effects leads to the large decrease in exothermicity (by 77.7−216.9 kJ mol^{-1}). Examination of stabilization energies calculated using eqs 2 and 3 in Table 3 shows that the major contribution to the stabilization of formylcarbene (115.5−116.5 kJ mol^{-1}) is provided by the OH or OMe substituents (acid or ester delocalization) while a smaller contribution (53.4−56.5 kJ mol^{-1}) is provided by the chloro or fluoro substituents (direct carbene stabilization).[44] When acting together in the derivatives of formylcarbene, these two stabilizing effects are slightly greater than additive (by 15.6−21.6 kJ mol^{-1}).

More specifically, we predict a large decrease in the exothermicity (to −177.5 kJ mol^{-1}) in going from formylcarbene

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(44) When comparing the effect of substituents on the relative energies of the carbonylcarbenes and ketenes, a key factor is that acid or ester stabilization is present in the former but not in the latter. Thus the difference in stabilization effects in **2-H** and **3-H**, for example, is very large when assessed in this way. In contrast, when assessing the effect of substituents on the singlet−triplet separation, the acid or ester stabilization is present for both the singlet and triplet forms of **2-H** and **3-H** (and of the reference molecule CH_3W in eq 1). The calculated substituent effect is simply measuring the effect of −CO−H or −CO−OH substituents on the stability of a carbene, and the difference in stabilizing effects in **2-H** and **3-H** is quite small from this viewpoint.

to carbohydroxycarbene (**3-H**) and a slight increase in the barrier (to 28.1 kJ mol^{-1}). Consistent with the reduced exothermicity, the transition structure is slightly later in **3-H**, with a $\angle$CCO angle of 135.6° and a $\angle$CC(OH) angle of 97.8°. Results for carbomethoxycarbene (**4-H**) are very similar in all respects to those for carbohydroxycarbene (**3-H**).

The effect of chloro substitution is to decrease the exothermicity for the Wolff rearrangement to -238.6 kJ mol^{-1} but to also decrease the barrier to 10.6 kJ mol^{-1} in formylchlorocarbene (**2-Cl**). The transition structure is later ($\angle$CCO = 148.1° and $\angle$CCH = 86.5°), as expected for a less exothermic reaction. Carbohydroxychlorocarbene (**3-Cl**) shows a significantly decreased exothermicity (reduced to -113.9 kJ mol^{-1}) and also the expected significantly increased barrier (64.2 kJ mol^{-1}) and later transition structure ($\angle$CCO = 155.1° and $\angle$CC(OH) = 76.5°).

The results for carbomethoxychlorocarbene (**4-Cl**) are again very similar to those for the carbohydroxy system. In particular, the calculated barrier for the Wolff rearrangement for **4-Cl** is 58.2 kJ mol^{-1}.

The results for the fluoro-substituted carbonyl carbenes (**2-F**, **3-F**, **4-F**) are closely related to those for the corresponding chloro systems (**2-Cl**, **3-Cl**, **4-Cl**) and the differences are readily rationalized. The exothermicities are about 10−30 kJ mol^{-1} less, the barriers are 10−12 kJ mol^{-1} larger, and the transition structures are slightly later in all cases. The largest relative difference occurs between **2-Cl** and **2-F**.

The Wolff rearrangement barriers generally increase with decreasing reaction exothermicity, as expected. The largest barriers occur for the least exothermic reactions, and involve halogeno and acid or ester substitutents that provide substantial stabilization to the carbene. The main exception to the barrier/exothermicity relationship is formylcarbene itself for which the barrier is significantly higher than might have been expected on the basis of its rearrangement exothermicity and the results for the remaining systems.

It is tempting to speculate why the barrier for the Wolff rearrangement of formylcarbene *is* significantly higher than expected on the basis of its exothermicity. A possible reason is the bridging stabilization in **2-H** that leads to the narrow $\angle$CCO angle of 96.1°. To obtain an approximate estimate of the magnitude of this effect, we have recalculated the G3(MP2)//B3-LYP barrier starting with a structure for **2-H** in which the $\angle$CCO angle is constrained to be 117.0° (a value between those in **2-Cl** (118.1°) and **2-F** (116.2°)) but all other parameters are optimized. Neglecting zero-point vibrational energy effects, the barrier is reduced to 8.8 kJ mol^{-1}, which is now consistent with the exothermicity. This result does indeed support the view that the barrier in **2-H** is anomalously high, particularly compared with the barriers in **2-Cl** and **2-F**, and suggests that this may be attributed to specific stabilization in **2-H**. This effect is also likely to be present but to a much smaller extent in **3-H** and **4-H**, i.e., the barriers in both these cases are slightly higher than expected on the basis of the calculated exothermicity because of bridging stabilization in the carbenes.[45]

It is of interest to examine existing experimental data in the light of the present theoretical results. Formylcarbene (**1-H**)[37] and carboethoxycarbene,[40] a close analogue of **4-H**, have been studied in solution by laser flash photolysis techniques using the pyridine ylide method. The formation of the ylides derived from these carbonyl carbenes was too fast to resolve by nanosecond spectroscopy. With the assumption that the absolute rate constants for the reactions of singlet formylcarbene and carboethoxycarbene with pyridine are $(1-5) \times 10^9$ M^{-1} s^{-1}, the lifetimes of both of these carbenes in solution were deduced to be on the order of hundreds of picoseconds. Because the carbene lifetimes in cyclohexane and cyclohexane-d_{12} were found to be very similar, it was concluded that the lifetimes of formylcarbene and carboethoxycarbene are controlled by an intramolecular process (Wolff rearrangement) rather than by reaction with solvent. Formylcarbene[37] was studied as a function of temperature and the barrier to its disappearance was found to be comparable to the barrier to the reaction of this carbene with pyridine, or ~8−10 kJ mol^{-1}. This is significantly smaller than the best calculated barrier obtained in the present study (18.5 kJ mol^{-1}, Table 4). We have probed whether this discrepancy is associated with a significant contribution from quantum mechanical tunneling by using Wigner's approximate formulation.[46,47] However, the estimate of the tunneling correction obtained in this manner is small, with an effective barrier lowering of less than 1 kJ mol^{-1}. On the other hand, our SCIPCM calculations indicate that solvation may make a nonnegligible contribution to the reaction barrier. Thus we find a barrier lowering as a function of dielectric constant of 2 (ϵ = 2) to 6 (ϵ = 40) kJ mol^{-1}. This brings the calculated barrier significantly closer to the experimental estimate.

The barriers to the disappearance of carbomethoxychlorocarbene (**4-Cl**) have been measured to be 5.5, 10.9 and 24.8 kJ mol^{-1} in trifluorotoluene, $CF_2ClCFCl_2$ (Freon-113), and perfluorohexane, respectively.[7] These values are much smaller than the calculated barrier to Wolff rearrangement of this carbene (58.2 kJ mol^{-1}) and suggest that the lifetimes of **4-Cl** in trifluorotoluene and Freon-113, and possibly perfluorohexane, are controlled in some measure by bimolecular processes.

Concluding Remarks

High-level ab initio calculations have been carried out for carbomethoxychlorocarbene and related systems. Attention has been focused on the singlet−triplet splittings and on the barrier for the Wolff rearrangement.

The parent carbonyl carbenes (**2-H**, **3-H**, **4-H**) are all predicted to have triplet ground states whereas the carbonyl chlorocarbenes (**2-Cl**, **3-Cl**, **4-Cl**) and carbonyl fluorocarbenes (**2-F**, **3-F**, **4-F**) all have singlet ground states.

Wolff rearrangement barriers for the parent carbonyl carbenes (**2-H**, **3-H**, **4-H**) lie in the range 25−30 kJ mol^{-1}. Chloro and fluoro substitution lead to a reduction in the Wolff rearrangement barriers for the formylcarbenes (**2**) but to an increase in the barriers for the carbohydroxy- (**3**) and carbomethoxy- (**4**) carbenes. The barriers generally correlate with exothermicity, the main exception being formylcarbene itself for which the calculated barrier is larger than would be expected on the basis of the very large exothermicity. The least exothermic reactions, corresponding to the Wolff rearrangement of the carbohydroxy- and carbomethoxy- chloro- and fluorocarbenes, have the highest barriers.

Acknowledgment. We gratefully acknowledge a generous allocation of time on the Fujitsu VPP300 and SGI Power

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[45] With $\angle$CCO angles constrained to be 117.0° in **3-H** and **4-H**, the calculated barriers (without ZPVE) are 25.4 and 21.3 kJ mol^{-1}, respectively. For the remaining systems, the barriers (without ZPVE) calculated from the structures with $\angle$CCO constrained to be 117.0° are 15.2 (**2-Cl**), 67.8 (**3-Cl**), 62.2 (**4-Cl**), 26.8 (**2-F**), 79.3 (**3-F**) and 74.9 (**4-F**) kJ mol^{-1}.

[46] See, for example: Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941; p 191.

[47] The change in the activation energy as a result of hydrogen tunneling is given by $E_a^* - E_a = -RT \ln \kappa$ where $\kappa = 1 + u^2/24$, $u = h\nu_i^{\#}/k_BT$ and $\nu_i^{\#}$ is the imaginary frequency at the saddle point.

Challenge computers of the Australian National University Supercomputing Facility.

Supporting Information Available: Calculated total energies (Table S1) and GAUSSIAN 98 archive entries for the B3-LYP/6-31G(d) and B3-LYP/cc-pVTZ+1 optimized geometries (Table S2) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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