

Structure and Energetics of Simple Carbenes CH₂, CHF, CHCl, CHBr, CF₂, and CCl₂

Charles W. Bauschlicher Jr.,^{1a} Henry F. Schaefer III,^{*1a} and Paul S. Bagus^{1b}

Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory,[†] University of California, Berkeley, California 94720, and IBM Research Laboratory, San Jose, California 95193. Received May 14, 1976

Abstract: There is very little experimental data concerning the singlet-triplet separations of carbenes. In many cases, it is not even possible to form estimates of this separation from experimental results. CH₂ is a distinct exception; here substantial, although contradictory, data are available. The equilibrium geometries of the lowest singlet states of several carbenes have been determined experimentally. However, the geometries of many states are not known and the triplet state geometries are also generally unknown. In order to obtain theoretical information about these quantities for a series of halogenated carbenes, we have studied CH₂, CHF, CHCl, CHBr, CF₂, and CCl₂ using a consistent level of ab initio electronic structure theory. One configuration (triplet state) and two configuration (singlet state) wave functions have been computed. Double ζ basis sets augmented by a d function on the carbon atom, optimized separately for both the singlet and triplet states of each molecule, were used. The theoretical equilibrium geometries agree well with the available experimental data. The trends of the singlet-triplet separations are discussed and correlated with the carbon atom Mulliken gross populations for the singlet and triplet states.

In recent years, one of the most interesting areas of experimental activity in organic chemistry has been carbene chemistry.² There has also been a considerable amount of theoretical research³⁻²² concerning the simplest carbene, the methylene free radical CH₂. These theoretical studies have complemented the experimental work and reliable information concerning the geometries, potential energy surfaces, and chemical reactions of the ground and excited electronic states of CH₂ is now available. Despite the importance of these studies, it is well to recall that in synthetic and mechanistic experimental studies substituted methylenes are often more convenient to use than the elementary CH₂ itself. As just one example, we point out that much of Skell's pioneering work²³ on the stereospecificity of carbene reactions was carried out using dibromocarbene, CBr₂. However, as was the case until very recently for CH₂, there is no quantitative experimental data for the singlet-triplet separation in CBr₂ and other halocarbenes. A knowledge of the singlet-triplet separation is essential to any reasonably complete understanding of the chemistry of a particular carbene. In the present paper, we report ab initio results for the structure and energetics of a series of halocarbenes CHX and CX₂.

Two conflicting sets of experimental values for the ³B₁-¹A₁ separation, ΔE , in CH₂ have been reported. The high values²⁴⁻²⁸ for ΔE are 8-9 kcal/mol (triplet state stable) and the low values²⁹⁻³¹ are 0-3 kcal/mol. Recent theoretical results^{18,32-35} have all supported the high values. However, the very recent laser photodetachment studies of Zittel et al.³⁶ yield an even larger separation, 19.5 ± 0.7 kcal/mol. This experiment is the only "direct" measurement; i.e., it does not depend in any way upon assumed thermochemical data. Thus their result³⁶ for ΔE could be the most accurate even though it differs substantially from all previously reported experimental values.²⁴⁻³¹

Among the molecules studied in the present research, CHF and CF₂ have been the subject of two previous theoretical studies.^{15,37} Of these, the more recent results of Staemmler¹⁵ are the more reliable. Using a double ζ plus polarization basis set, Staemmler carried out SCF and pair correlation studies of CHF and CF₂. With fixed bond distances $r(\text{CH}) = 1.11$ Å and $r(\text{CF}) = 1.30$, he predicted the bond angles of the lowest singlet and triplet states, and the singlet-triplet separations, -11 (CHF) and -47 kcal (CF₂), with the singlet state lying

lower in both cases. These separations are not known from experiment. However, the ground state singlet structures of CHF³⁸ [$r(\text{CF}) = 1.314$ Å, $r(\text{CH}) = 1.121$ Å, $\theta = 101.6^\circ$] and CF₂³⁹⁻⁴¹ [$r(\text{CF}) = 1.300$ Å, $\theta = 104.9^\circ$] are known. The structure of the lowest singlet state of CHCl is also known from experiment,⁴² $r(\text{CCl}) = 1.689$ Å, $r(\text{CH}) = 1.12$ Å, $\theta = 103.4^\circ$. Although electronic spectra have been recorded for all three molecules, no triplet state transitions have been identified.

Although CCl₂ and CBr₂ have been studied extensively by matrix isolation spectroscopy,⁴³⁻⁴⁵ their molecular structures are not known. Although the ΔE values are also not known, a singlet ground state is presumed based on the failure to observe nonstereospecificity in the addition reactions to olefins.⁴⁶ Neither the vibrational nor electronic spectrum of the CHBr molecule has been observed. However, CHBr is readily generated from the corresponding diazo compound and its reactions have been investigated in some detail.^{2,47}

Theoretical Approach. The present research builds upon previous theoretical work^{22,32-35} on CH₂ which suggests that quite reliable structures and reasonable singlet-triplet separations may be obtained from rather simple wave functions. For CH₂, the triplet state is approximately described by a single determinant self-consistent field (SCF) wave function.

$$1a_1^2 2a_1^2 1b_2^2 3a_1 1b_1; {}^3B_1 \quad (1)$$

The singlet state requires a two-configuration SCF description.

$$c_1 1a_1^2 2a_1^2 1b_2^2 3a_1^2 + e_2 1a_1^2 2a_1^2 1b_2^2 1b_1^2 \quad {}^1A_1 \quad (2)$$

The key feature of this approach is that it treats the 3a₁ and 1b₁ orbitals on an equal footing for both electronic states. Near the Hartree-Fock limit (saturated basis set), this level of theory predicts²² 10.9 kcal/mol for ΔE . This value is reasonably close to that obtained from the best available configuration interaction (CI) result³³ ($\Delta E = 14.1$ kcal/mol; the same authors estimate the true ΔE value to be 11 ± 2 kcal). It is also quite close to the 8-9 kcal experimental values;²⁴⁻²⁸ however, it is considerably smaller than the experimental value obtained by Zittel et al.,³⁶ $\Delta E = 19.5 \pm 0.7$ kcal/mol. In fact, their result is closer to the separation obtained when one-configuration SCF wave functions are used for both the ³B₁ and ¹A₁ states; this computed separation²² is 24.8 kcal/mol.

For all the carbenes considered in the present paper, the triplet (one configuration) and singlet (two configurations)

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Table I. Dunning's Contracted Gaussian Basis Set for the Bromine Atom^a

[8s] set		[6p] set		[2d] set	
s exponents	Coefficients	p exponents	Coefficients	d exponents	Coefficients
439 700.	0.000 813	2957.	0.022 262	134.8	0.018 309
66 030.	0.006 285	700.3	0.180 188	36.39	0.135 002
15 140.	0.031 923	224.6	0.862 405	12.16	0.426 091
4 317.	0.128 793	82.59	0.343 999	4.341	0.604 271
1 414.	0.394 591	33.19	0.507 099	1.535	1.000 000
523.9	0.541 292	14.20	0.258 957		
523.9	0.183 066	14.20	0.079 647		
207.7	0.617 646	7.438	0.373 442		
86.54	0.253 828	3.526	0.604 912		
30.52	1.000 000	1.595	1.000 000		
12.98	1.000 000	0.4918	1.000 000		
4.412	1.000 000	0.1507	1.000 000		
1.862	1.000 000				
0.5455	1.000 000				
0.1902	1.000 000				

^a The notation used follows ref 48.

wave functions are the appropriate analogues of eq 1 and 2. (Of course CHF, CHCl, and CHBr have only a plane of symmetry and hence the corresponding term symbols are ³A'' and ¹A'.) The use of a two-configuration singlet and one-configuration triplet description provides a consistent picture of the singlet-triplet separation. With this relatively simple model, a study of this extended series of carbenes was computationally feasible.

The basis sets used here begin with Dunning's contracted Gaussian double ζ sets. For hydrogen we use his (4s/2s) contraction⁴⁸ of Huzinaga's primitive set⁴⁹ (with a scale factor of 1.2); for carbon and fluorine the (9s 5p/4s 2p) contraction of Huzinaga's primitive set; for chlorine the (12s 9p/6s 4p) contraction⁵⁰ of Veillard's primitive set;⁵¹ and for bromine Dunning's (14s 11p 5d/8s 6p 2d) contraction of his own primitive set.⁵² Since Dunning's bromine basis has never been used or reported in the literature previously, it is given in Table I. These double ζ bases are sufficiently flexible to allow reasonably accurate SCF descriptions of the separated atoms. The calculated, ground-state atomic SCF energies, in hartrees, with extended Slater basis near Hartree-Fock values⁵³ in parentheses, are as follows: H(2S) -0.4993 (-0.5); C(3P) -37.6845 (-37.6886); F(2P) -99.3933 (-99.4093); Cl(2P) -459.4706 (-459.4819); and Br(2P) -2572.3102 (-2572.4408). With these basis sets, we varied both lengths and angles to obtain equilibrium geometries for each of the carbenes considered.

To the double ζ basis set we added a d function centered on carbon. All six Cartesian components ($x^2e^{-\alpha r}$, $xye^{-\alpha r^2}$, $xze^{-\alpha r^2}$, $y^2e^{-\alpha r^2}$, etc.) were retained in the basis set. For CH₂, we simultaneously optimized both the geometry and the d function exponent α . The optimum α for the ³B₁ state was 0.74; for the ¹A₁ state, it had the quite different value $\alpha = 0.51$. For the other carbenes, except CHBr, the singlet and triplet geometries were optimized using these CH₂ d function exponents. Then, at the computed equilibrium geometries, the values of α were reoptimized for each carbene. For reasons of economy, this procedure was simplified for the CHBr molecule. There the singlet and triplet geometry optimizations were carried out only at the double ζ level. Final computations were performed at these two geometries using carbon d functions with orbital exponent $\alpha = 0.4$. This exponent was chosen based on the trends of optimized values for the other systems. In Table II, we give the equilibrium geometries, total energies, and mixing coefficients (c_1 and c_2 of eq 2), and singlet-triplet separations obtained using these basis sets.

For CH₂ and CF₂, we also used more extended basis sets and optimized the geometry for these sets. The results obtained are

reported in Table II. For CH₂, the addition of a set of p functions ($\alpha = 1.0$) to each hydrogen changes the singlet-triplet separation from 12.3 and 12.8 kcal/mol. For both the singlet and triplet state, geometry changes are minor (bond distances change by less than 0.005 Å and bond angles by less than 1°). For difluorocarbene, the addition of a set of d functions ($\alpha = 1.0$) on each F atom changes ΔE from -45.3 to -44.5 kcal. Here, however, the addition of d functions changes the bond distance more substantially. For example, the calculations including polarization functions only on carbon give $r_e(\text{CF}) = 2.477 \mu_B$ and $\theta_e = 117.8^\circ$ for the ³B₁ state. Upon addition of polarization functions to the fluorine atoms, these change to $r_e(\text{CF}) = 2.463 \mu_B$ and $\theta_e = 118.2^\circ$ and the total energy is lowered by 0.024 hartree. Thus it is probably true that the absence of polarization functions on the terminal atoms becomes a more serious problem as one goes from CH₂ to CF₂ to CCl₂ to CBr₂. Note also that for CF₂ the carbon d exponents were reoptimized after adding the fluorine polarization functions, yielding $\alpha = 0.69$ for the ³B₁ state and $\alpha = 0.67$ for the ¹A₁ state.

Results and Discussion

We turn first to an evaluation of the molecular structures, since there is a fair amount of experimental data available for these. In Table III, we summarize the computed equilibrium geometries for the singlet and triplet states of the carbenes obtained using the double ζ plus optimized carbon d function basis sets. Experimental values, where available, are included for comparison.

For all four experimentally known bond angles, the singlet states of CH₂, CHF, CHCl, and CF₂, the theoretical predictions are in close agreement with experiment, the differences being 0.1, 0.6, 1.4, and 0.6°. The best existing theoretical calculations^{33,35} for the ³B₁ state of CH₂ give a bond angle near 134° while our SCF result is 129°. An accurate value for this bond angle is not available from experimental studies. However, matrix isolation EPR measurements⁵⁴ and a reinterpretation of the vacuum ultraviolet absorption spectrum⁵⁵ support a value⁵⁴ of $136 \pm 5^\circ$. The apparently large error of our calculated SCF bond angle is probably a result of the fact that the ³B₁ CH₂ potential surface is fairly flat near equilibrium. It is interesting to note that Zittel et al.³⁶ report a still larger bond angle of $138 \pm 4^\circ$. This value is obtained by adjusting computed potential surfaces to fit the observed CH₂-photodetachment spectrum.

For CH₂, CHF, and CHCl, the predicted CH bond distances agree well with experiment, the errors being 0.004,

Table II. Equilibrium Geometries, Total Energies, and Singlet-Triplet Separations for Various Basis Sets for a Number of Simple Carbenes^a

Molecule	Basis set	S-T separation, kcal/mol	Triplet carbene				Singlet carbene							
			Orb exp	r(CH)	r(CX)	θ	E(total)	Orb exp	R(CH)	r(CX)	θ	E(total)	c ₁	c ₂
CH ₂	No polarization functions	23.0	0.741	1.074	1.350	118.6	-38.913 69	0.511	1.099	1.347	103.5	-38.891 45	0.9862	-0.1655
	Optimized d function on C	12.3	0.741	1.075	1.311	117.8	-38.923 74	0.511	1.106	1.305	102.5	-38.904 11	0.9795	-0.2014
CF ₂	d function on C; p on H _b	12.8	0.741	1.074	1.303	118.2	-38.928 22	0.511	1.103	1.291	102.8	-38.907 87		
	No polarization functions	-31.9	0.741	1.074	1.350	118.6	-236.595 85	0.511	1.103	1.347	103.6	-236.646 63	0.9862	-0.1655
	d on carbon	-43.8	0.65	1.074	1.311	117.8	-236.648 52	0.64	1.103	1.305	104.3	-236.718 24		
	Optimized d on C	-45.3	0.741	1.074	1.311	117.8	-236.649 61	0.511	1.103	1.305	104.3	-236.721 85		
CCl ₂	d on C and d ($\alpha = 1.0$) on F	-44.5	0.741	1.074	1.303	118.2	-236.673 26	0.511	1.103	1.291	104.7	-236.744 23	0.9842	-0.1768
	Optimized d on C and d on F ^b	-46.5	0.69	1.074	1.303	118.2	-236.673 42	0.67	1.103	1.291	104.7	-236.747 21		
	No polarization functions	-2.9	0.741	1.074	1.771	126.0	-956.707 34	0.511	1.103	1.830	109.5	-956.712 02	0.9852	-0.1716
CHF	d on carbon	-17.9	0.45	1.074	1.730	125.5	-956.733 10	0.42	1.103	1.756	109.4	-956.761 61	0.9820	-0.1890
	Optimized d on C	-13.5	0.45	1.074	1.730	125.5	-956.741 87	0.42	1.103	1.756	109.4	-956.763 48	0.9863	-0.1647
CHCl	No polarization functions	1.7	0.66	1.074	1.366	120.7	-137.758 22	0.511	1.103	1.373	101.9	-137.755 45	0.9824	-0.1866
	d on carbon	-7.2	0.741	1.077	1.324	120.1	-137.787 70	0.61	1.111	1.325	102.2	-137.799 20	0.9859	-0.1671
CHBr	Optimized d on C	-9.2	0.66	1.077	1.321	120.4	-137.788 13	0.46	1.103	1.325	102.2	-137.802 72	0.9813	-0.1924
	No polarization functions	9.2	0.741	1.075	1.779	123.8	-497.814 18	0.511	1.103	1.840	101.9	-497.799 59	0.9863	-0.1649
CHBr	d on carbon	-3.5	0.49	1.075	1.735	123.3	-497.831 91	0.46	1.103	1.762	102.0	-497.837 77	0.9813	-0.1924
	Optimized d on C	-1.6	0.49	1.075	1.735	123.3	-497.835 24	0.46	1.103	1.762	102.0	-497.837 77	0.9863	-0.1649
CHBr	No polarization functions	12.4	0.40	1.075	1.891	125.6	-2610.650 07	0.40	1.103	1.972	102.6	-2610.632 16	0.9812	-0.1929
	d on carbon	1.1	0.40	1.075	1.891	125.6	-2610.671 56	0.40	1.103	1.972	102.6	-2610.669 77	0.9812	-0.1929

^aThe orbital exponents of the carbon d functions are tabulated and the configuration mixing coefficients, c_1 and c_2 , (cf. eq 2), are given for representative cases for each carbene. A negative singlet-triplet separation indicates a singlet ground state. Bond lengths are in Å, and total energies in hartrees. $b_{\alpha} = 1.0$.

0.010, and 0.019 Å. As already noted for the bond angles, the errors of the calculated bond lengths become larger for the carbenes which contain heavier halogen atoms. This trend is more apparent for the CCl bond distance for the ¹A' state; our ab initio value, 1.76 Å, is a full 0.07 Å longer than experiment. We suspect that the use of polarization functions (i.e., a single set of d functions) on chlorine would remove most of this error. By comparison, for the ClF₂ molecule, Ungemach and Schaefer⁵⁶ find that the addition of d functions on Cl decreases the predicted bond distances by 0.10 Å. Finally, we note that the C-F distances in singlet CHF and CF₂ are predicted in very good agreement with experiment.

For the reasons mentioned in the previous paragraph, we expect the calculated CCl distance in CCl₂ to be ~0.1 Å larger than the exact (unknown) bond distance. Similarly, the calculated CBr distance in CHBr is expected to be somewhat larger than the Hartree-Fock limit (complete basis set) result. In addition, for CHBr the lack of a geometry optimization with carbon d functions also will have some effect. Comparisons for CHCl suggest that the CH distance and bond angle are relatively independent of the carbon polarization functions. However, the CCl distances in singlet and triplet CHCl were reduced by 0.08 and 0.04 Å, respectively, by geometry optimization with carbon d functions. We expect that the accuracy of the computed equilibrium geometries for the triplet states will be the same as for the singlet states discussed above.

Inspection of Table III shows several fairly clear trends. Perhaps the most obvious is the fact that the singlet bond angles are much smaller than their triplet counterparts. Less obvious but consistent with the above is the observation that with one exception (CF₂) the triplet carbene bond distances are smaller than those of the corresponding singlet states. The magnitudes of the triplet bond angles span a fairly narrow range, from 117.8 (CF₂) to 128.8° (CH₂). The same is true of the singlet bond angles, which vary from 102.0 (CHCl) to 109.4° (CCl₂). The triplet bond angles are close to the 120° appropriate to sp² hybridization on the carbon atom. The fourth carbon electron is, of course, in the singly occupied p_z (b₁ or a'') orbital normal to the plane of the molecule. The singlet bond angles are close to 90° which would be appropriate for a 2s²2p_x1²p_y1 hybridization. As we shall show later, this interpretation is supported by Mulliken population analyses of the charge on the carbon atom. Clearly, the singlet and triplet carbenes have quite different geometries.

Turning to the singlet-triplet separations, it appears clear that CF₂ and CCl₂ have ¹A₁ ground states. For CF₂ the separation is quite large, with the singlet lying ~45 kcal lower. CCl₂ is more uncertain owing to the potential importance of Cl polarization functions but -14 kcal is a plausible estimate. For CHF, CHCl, and CHBr definitive predictions of the ground states are more difficult; the theoretical predictions are -9 kcal (singlet lower) for CHF, -2 kcal (singlet lower) for CHCl, and 1 kcal (triplet lower) for CHBr.

Between CH₂ (triplet stable) and CF₂ (singlet stable) there is variation of 57 kcal in the relative stabilities of the singlet and triplet states. It would be very helpful if this range of stability could be correlated to the electronegativity of the halogen member of the carbene and to the computed distribution of charge on the carbon atom. In order to provide a basis for this correlation, we give, in Table IV, Mulliken populations for the molecules studied along with calculated and estimated values of the singlet-triplet separations. The gross atomic and valence populations on carbon are given for both the singlet and triplet states. The valence population is divided into 2s (total s population - 2 1s shell electrons) and 2p character. (Mulliken populations should only be used for qualitative comparisons since they tend to be basis dependent. For this reason the populations given in Table IV are those obtained with the straight double ζ basis sets which have no polarization func-

Table III. Summary of Computed Equilibrium Geometries for Some Simple Carbenes^f

Molecule	Triplet carbene			Singlet carbene		
	<i>r</i> (CH)	<i>r</i> (CX)	θ	<i>r</i> (CH)	<i>r</i> (CX)	θ
CH ₂	1.075		128.8	1.106 (1.11 ^a)		102.5 (102.4 ^a)
CHF	1.077	1.321	120.4	1.111 (1.121 ^b)	1.325 (1.314 ^c)	102.2 (101.6 ^c)
CHCl	1.075	1.735	123.3	1.101 (1.12 ^d)	1.762 (1.689 ^d)	102.0 (103.4 ^d)
CHBr	1.075	1.891	125.6	1.103	1.972	102.6
CF ₂		1.311	117.8		1.305 (1.300 ^e)	104.3 (104.9 ^e)
CCl ₂		1.730	125.5		1.756	109.4

^a G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1967. ^b Assumed. ^c Reference 38. ^d Reference 42. ^e Reference 41. ^f Bond distances are reported in Å and bond angles in degrees. The results in this table were obtained using double ζ basis sets augmented by an optimized d function on the carbon atom. Experimental values are given in parentheses.

Table IV. Mulliken Populations and Singlet-Triplet Separations Δ*E* for Several Carbenes^a

	Triplet population			Singlet population			<i>R</i> ₁	<i>R</i> ₂	Calcd Δ <i>E</i> , kcal/mol
	Total	2s	2p	Total	2s	2p			
CH ₂	6.36	1.43	2.93	6.25	1.71	2.53	1.20	1.23	+12.8
CHBr	6.25	1.48	2.77	6.13	1.83	2.30	1.24	1.27	+1.1
CHCl	6.14	1.45	2.69	6.03	1.81	2.21	1.25	1.29	-1.6
CHF	5.85	1.33	2.53	5.77	1.72	2.05	1.29	1.32	-9.2
CCl ₂	5.99	1.45	2.53	5.89	1.87	2.02	1.29	1.32	-13.5
CF ₂	5.39	1.12	2.28	5.41	1.69	1.71	1.51	1.51	-44.5

^a The calculated values of Δ*E* are those obtained with the basis set which includes optimized carbon d functions. The quantities *R*₁ and *R*₂ are ratios of 2s and 2p populations for the singlet and triplet states and are defined in eq 3 and 4.

tions included.) The total carbon populations are nearly the same, within 0.1 electron, for the singlet and triplet states of each carbene. The division into 2s and 2p character is, however, quite different. For the triplet states, the 2s population varies from 1.12 (CF₂) to 1.43 (CH₂) suggesting a carbon hybridization approaching sp² (with an additional singly occupied p_z orbital) and consistent with the computed bond angles near 120° (cf. Table III). For the singlet states, the 2s and 2p populations are more nearly equal and usually close to 2 consistent with a hybridization approaching s²p_xp_y and nearly 90° bond angles.

The singlet-triplet separation correlates with the total charge on carbon. When carbon has a negative charge, the carbene is triplet stable; when it has a positive charge, the carbene is singlet stable. Both chemical intuition and the observed Mulliken populations suggest that fluorine is more electronegative than chlorine, and chlorine more so than bromine. The singlet-triplet separation is greatest for CF₂, and CCl₂ is also predicted to have a ground-state singlet. Although we did not perform comparable studies of CBr₂, it seems likely that the ¹A₁ and ³B₁ states will be nearly degenerate, lying within a few kcal of each other. In light of the greater reactivity^{14,20,21} of singlet carbenes, it is not surprising that CBr₂ appears to have the characteristics of a ground-state singlet.²³ The CHX species exhibit the same general trend.

The dependence of the singlet-triplet separation on the charge on carbon can be understood in terms of the very different hybridization for the singlet and triplet states. In order to form an sp² hybrid a rather large promotion energy is required; the energy difference⁵⁷ between C(2s² 2p²; ³P) and C(2s2p³; ⁵S) is 4.2 eV. This promotion energy is compensated by the strength of the bonds formed with the sp² hybrids. When the carbon is negatively charged, as in the case for CH₂, CHBr, and CHCl, some of the charge goes into the atomic 2s orbital reducing the "promotion energy". When electrons are removed from carbon by strongly electronegative neighbors (the case for CHF, CCl₂, and CF₂), the "promotion energy" is increased. For example, the energy difference⁵⁷ between C⁺(2s²2p²; ²P) and C⁺(2s2p²; ⁴P) is 5.3 eV. In this case, the triplet becomes less stable with respect to the singlet state. For the singlet

states, the 2s population is much closer to 2 and the promotion energies are correspondingly smaller than for the triplets. Of course, the bonds formed are also relatively weaker. We can form two ratios to measure the relative values of the promotion energies for the singlet and triplet states:

$$R_1 = \frac{\text{singlet 2s population}}{\text{triplet 2s population}} \quad (3)$$

and

$$R_2 = \frac{\text{singlet 2s pop/singlet (2s + 2p) pop}}{\text{triplet 2s pop/triplet (2s + 2p) pop}} \quad (4)$$

The smaller the ratio, the smaller the promotion energy difference will be between the triplet and singlet states. Hence, the triplet state will be more stable than the singlet. The reverse will be true for larger ratios. The values of *R*₁ and *R*₂ are given in Table IV and the expected behavior is, indeed, followed.

Goddard et al.⁵⁸ have considered qualitatively the relative stability of the singlet and triplet states for CH₂ and CF₂ using a valence bond analysis. Their arguments are directly related to the excitation energies of the ⁴Σ⁻ STATES OF CH and CF. In order to form the triplet state of CX₂ (X = H or F), they find that one C-X bond must be like that in the ⁴Σ⁻ state of the corresponding diatomic molecule. The other C-X bond is like that in the ground ²Π state. For the singlet state of CX₂, both C-X bonds are like that in the ²Π state. The ⁴Σ⁻ state of CH is close to, ~0.5 eV above, the ²Π state,^{59,60} the ⁴Σ⁻ state of CH is highly excited,⁵⁸ ~3 eV above ²Π. Thus the triplet state of CF₂, which requires a ⁴Σ⁻-like bond, is expected to be considerably higher than the singlet state. This is found to be the case in our calculations and in previous work.^{15,37}

However, a simple extension of the arguments of Goddard et al.⁵⁵ does not explain the different singlet-triplet separations found for CH₂ and CHF. In both the singlet and triplet states of CHF, the C-F bond would be the favorable ²Π-like bond; only the C-H bond would change from ⁴Σ⁻-like (triplet CHF) to ²Π-like (singlet CHF). Thus CH₂ and CHF would be expected to have similar singlet-triplet separations. In this and previous work,^{15,37} however, these separations are found to be quite different; in every case, Δ*E*_{ST}(CH₂) - Δ*E*_{ST}(CHF) is

found to be ~ 22 kcal/mol. Our correlation of the singlet-triplet separation with the Mulliken atomic populations for C (and hence the electronegativity of the halogen substituent) is able to account for the separation in CHF as well as in CF₂.

Finally, we note that all of the above halocarbenes (plus CBr₂) have been studied by Hoffman, Zeiss, and Van Dine⁶¹ using extended Hückel theory. These authors emphasize that their results should be taken qualitatively. In fact, many of the trends reported here are seen in this earlier semiempirical study.

Note Added in Proof. We have recently (unpublished) carried out very large scale CI studies of the CH₂ singlet-triplet separation. It now seems clear that the ΔE value of 11 ± 2 kcal predicted in ref 33 is correct. This conclusion greatly strengthens the credibility of the much simpler molel studies reported in the present paper.

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