

Ground-State Multiplicity of Halo(trifluoromethyl)carbenes

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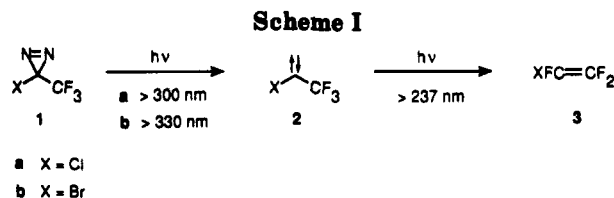
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The recent report of O'Gara and Dailey¹ prompts us to describe related studies concerning chloro(trifluoromethyl)carbene (**2a**) and bromo(trifluoromethyl)carbene (**2b**). Our interest in these molecules stems from our desire to prepare an unusual type of carbene: a heteroatom-substituted carbene possessing a triplet electronic ground state. These two features are generally mutually exclusive.² With the recent exception of HCl,³ all experimental evidence concerning heteroatom-substituted carbenes suggests that they possess singlet electronic ground states.⁴ Nevertheless, *ab initio* calculations predict either singlet ground states (S_0) with small singlet-triplet energy splittings (ΔE_{ST})⁵ or triplet ground states (T_0) for HCCl,^{6,7} HCB, ^{6b,7} HCl, ^{6b} Cl₂, ^{6b} BrCCF₃,¹ and XCSiH₃ (X = F, Cl, Br, I).^{6b} Substitution of CF₃ for H at a carbene center is predicted to have little effect on the singlet-triplet energy gap.⁸ Given the inherent difficulties in accurately predicting the ground-state multiplicity when the computed singlet-triplet splitting is small, we sought to determine experimentally the electronic ground state for chloro(trifluoromethyl)carbene (**2a**) and bromo(trifluoromethyl)carbene (**2b**) by electron spin resonance (ESR) spectroscopy. We do not observe triplet ESR signals for carbenes **2a** and **2b**; thus, we conclude that these species possess singlet electronic ground states. Our observations support the conclusions reached by O'Gara and Dailey on the basis of UV/visible spectroscopy.¹

Results and Discussion

Photolysis ($\lambda > 300$ nm) of 3-chloro-3-(trifluoromethyl)diazirine (**1a**), matrix-isolated in argon at 10 K, produces chloro(trifluoromethyl)carbene (**2a**)⁹ and a small amount of chlorotrifluoroethylene (**3a**) (Scheme I). The infrared spectrum of ClCCF₃ (**2a**) agrees with that reported by O'Gara and Dailey.¹ ESR spectra recorded after the



photolysis show no triplet transitions. On this basis, we conclude that ClCCF₃ (**2a**) possesses a singlet ground electronic state. Subsequent photolysis ($\lambda > 237$ nm) of carbene **2a** rapidly produces chlorotrifluoroethylene (**3a**), assigned by comparison with the infrared spectrum reported by Mann et al.^{10a}

Similarly, photolysis ($\lambda > 330$ nm) of 3-bromo-3-(trifluoromethyl)diazirine (**1b**), matrix-isolated in argon or xenon at 10 K, produces bromo(trifluoromethyl)carbene (**2b**)⁹ and a trace of bromotrifluoroethylene (**3b**) (Scheme I). The infrared spectrum of BrCCF₃ (**2b**) agrees with that reported by O'Gara and Dailey.¹ ESR spectra recorded during and after the photolysis show no triplet transitions. We therefore conclude that BrCCF₃ (**2b**) also possesses a singlet ground electronic state. Given the anticipated small singlet-triplet energy splitting in BrCCF₃ (**2b**), we felt that the triplet state might be thermally accessible at higher temperatures. ESR spectra recorded after warming carbene **2b** to 34 K in argon or 73 K in xenon, however, yielded no triplet signals. 1,2-Fluorine migration does not occur thermally at 73 K in xenon, as we did not observe growth of bromotrifluoroethylene (**3b**) by infrared spectroscopy.¹¹ Photolysis ($\lambda > 237$ nm) of BrCCF₃ (**2b**) in an argon or xenon matrix at 10 K rapidly produces bromotrifluoroethylene (**3b**), assigned by comparison with the infrared spectrum reported by Mann et al.^{10b}

Theory and experiment agree that the magnitude of the singlet-triplet energy splitting, ΔE_{ST} ,⁵ decreases along the series HCF > HCCl > HCB > HCl. Given the small singlet-triplet splittings computed for HCB (4 ± 2 kcal/mol) and HCl (0.8 ± 2 kcal/mol),^{6b} theory does not offer an unambiguous prediction for the multiplicity of the ground electronic state. Recent experiments by Lineberger and co-workers suggest that HCB possesses a singlet ground state ($\Delta E_{ST} = 2.6 \pm 2.2$ kcal/mol) and that HCl possesses a triplet ground state ($\Delta E_{ST} = -2$ to -10 kcal/mol).³ Dixon compared the singlet-triplet gaps (ΔE_{ST}) for HCH vs HCCF₃ and FCH vs FCCF₃ and found that substitution of H by CF₃ produced no significant changes in ΔE_{ST} .⁸ Thus, we viewed BrCCF₃ as an interesting carbene to study in light of the expected small singlet-triplet gap, the possibility of a triplet ground state, and the straightforward synthetic route to the diazirine precursor **1b**. Our ESR study shows conclusively that both **2a** and **2b** have singlet ground states, corroborating the conclusion reached by O'Gara and Dailey from UV/vis data.¹

Our inability to observe a triplet signal from BrCCF₃ (**2b**) at 73 K in xenon indicates that the triplet state is not

(1) O'Gara, J. E.; Dailey, W. P. *J. Am. Chem. Soc.* 1992, 114, 3581-3590.

(2) (a) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* 1978, 100, 1333-1338. (b) Mueller, P. H.; Rondan, N. G.; Houk, K. N.; Harrison, J. F.; Hooper, D.; Willen, B. H.; Liebman, J. F. *J. Am. Chem. Soc.* 1981, 103, 5049-5052.

(3) Gilles, M. K.; Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* 1992, 96, 1130-1141.

(4) For leading references, see: (a) Dixon, D. A.; Arduengo, A. J., III. *J. Phys. Chem.* 1991, 95, 4180-4182. (b) Sheridan, R. S.; Moss, R. A.; Wilk, B. K.; Shen, S.; Wlostowski, M.; Kesselmayr, M. A.; Subramanian, R.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* 1988, 110, 7563-7564. (c) Moss, R. A. *Acc. Chem. Res.* 1989, 22, 15-21.

(5) $\Delta E_{ST} = E_T - E_S$. Using this convention, negative values imply a triplet ground state and positive values imply a singlet ground state.

(6) (a) Carter, E. A.; Goddard, W. A., III. *J. Phys. Chem.* 1987, 91, 4651-4652. (b) Irikura, K. K.; Goddard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* 1992, 114, 48-51.

(7) (a) Bauschlicher, C. W., Jr.; Schaefer, H. F., III; Bagus, P. S. *J. Am. Chem. Soc.* 1977, 99, 7106-7110. (b) Scuseria, G. E.; Duran, M.; MacLagan, R. G. A. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* 1986, 108, 3248-3253.

(8) Dixon, D. A. *J. Phys. Chem.* 1986, 90, 54-56.

(9) Chloro(trifluoromethyl)carbene (**2a**): IR (Ar, 10 K) 1239 s, 1188 s, 1155 vs, 920 m, 793 w, 640 w, 544 w, 536 cm⁻¹. Bromo(trifluoromethyl)carbene (**2b**): IR (Ar, 10 K) 1229 s, 1179 s, 1148 s, 858 m, 746 w, 626 w, 543 w, 524 w cm⁻¹.

(10) (a) Mann, D. E.; Acquista, N.; Plyler, E. K. *J. Chem. Phys.* 1953, 21, 1949-1953. (b) Mann, D. E.; Acquista, N.; Plyler, E. K. *J. Chem. Phys.* 1954, 22, 1199-1202.

(11) Photolysis of diazirine **1b** ($\lambda > 330$ nm) in either a methylcyclohexane glass or a poly(chlorotrifluoroethylene) glass at 94 K failed to produce any ESR transitions associated with a triplet species. Unfortunately, we do not know whether the singlet carbene, if formed, is thermally stable in these matrices at 94 K.

thermally accessible at this temperature. O'Gara and Dailey calculated $\Delta E_{ST} = 0.5$ kcal/mol for **2b** using a DZ + P(2P₀) basis set and applying an empirical correction.¹ Using the Boltzmann distribution, we calculate the ratio of the thermal populations for two states separated in energy by 0.5 kcal/mol at 73 K to be $N_{\text{triplet}}/N_{\text{singlet}} = 0.10$.¹² Given the inherent sensitivity of ESR spectroscopy, we should be able to detect a triplet in this case. Thus, our results suggest that the triplet state of **2b** lies higher than 0.5 kcal/mol above the singlet.

In summary, we generated matrix-isolated chloro-(trifluoromethyl)carbene (**2a**) and bromo-(trifluoromethyl)carbene (**2b**) by photolysis of their diazirine precursors. ESR spectra of carbenes **2a** and **2b** at 16 K show no triplet transitions, revealing that these carbenes have singlet ground electronic states. ESR spectra of **2b** at 73 K in xenon indicate that the triplet state is not thermally accessible. Our efforts to characterize a ground-state triplet carbene bearing a heteroatom continue.

Experimental Section

Infrared spectra were obtained on a Nicolet 740 FTIR instrument (MCT-B detector). ESR experiments were performed at X-band (ca. 9.2 GHz) on either a Varian E-15 or a Bruker ESP-300 spectrometer. An EIP microwave counter (Model 625A CW) provided the microwave frequency. ¹H NMR spectra were obtained with a Bruker WP-200 spectrometer. Chemical shifts are reported as ppm downfield from internal Me₄Si. Mass spectral data were obtained with a Kratos MS-80RFA spectrometer (DS55/DS90 detector).

The glasses for the low-temperature ESR experiments were prepared in the following manner. Gaseous bromo-(trifluoromethyl)diazirine (**1b**) was transferred to a vacuum manifold of known volume. After the pressure was recorded, the diazirine was condensed into a sample tube at 77 K. The tube was warmed to -131 °C (pentane slush), filled with argon, and covered with a septum. A known volume of degassed methylcyclohexane (MCH, spectrophotometric grade, Aldrich) or poly(chlorotrifluoroethylene) (PCTFE, Polysciences) was added to the tube via syringe to produce a solution of known concentration (typically 0.1 M). The tube was placed in a cold bath (-78 °C for MCH solutions, 0 °C for PCTFE solutions) and gently rocked back and forth to dissolve the diazirine. Infrared spectra of the resulting solutions confirmed the presence of **1b**. Approximately 0.4 mL of solution was transferred to a quartz ESR sample tube (purged with argon and capped with a septum) via syringe. The tube was maintained at -78 °C. The MCH glass was formed by rapidly cooling the ESR tube in liquid N₂. The tube was quickly transferred to a precooled (94 K) ESR cavity. Because of the difficulty in degassing PCTFE, it was necessary to form the glass by slowly cooling the ESR tube from 195 K (dry ice-acetone) to 94 K in increments of 20 K, in the ESR cavity.

(12) This analysis assumes the triplet state to be triply degenerate, i.e., that the zero-field splitting of the triplet state is negligible at 73 K.

Matrix-Isolation Spectroscopy. The apparatus and experimental technique for low-temperature matrix-isolation spectroscopy have been described elsewhere.¹³ Irradiations were carried out with an ILC Technology LX300UV 300-W high-pressure xenon arc lamp. Wavelength control was provided by glass cutoff filters (<0.1% transmittance of wavelengths shorter than the specified values): Corning 0-52 (>330 nm), Schott WG-320 (>300 nm), Corning 0-56 (>237 nm).

Trifluoroacetamide. Trifluoroacetamide, CF₃C(NH)NH₂, was prepared in a two-step sequence. CF₃C(O)NH₂ (Fairfield, recrystallized from CH₂Cl₂) was dehydrated by P₂O₅ at 145 °C to produce CF₃CN, according to the procedure of Gilman and Jones.¹⁴ CF₃CN was then condensed in liquid NH₃ and refluxed to yield CF₃C(NH)NH₂.¹⁵ Excess NH₃ was removed by evaporation at room temperature followed by freeze-pump-thaw cycles at -30 °C: ¹H NMR (CDCl₃) δ 5.41 (br s); IR (neat) 3498 w-m, 3355 m, 3185 m, 1678 s, 1469 m, 1199 s, 1157 s cm⁻¹; mass spectrum *m/z* (relative intensity) 113 (M⁺ + 1, 3), 112 (M⁺, 100), 96 (14), 77 (8), 76 (23).

CAUTION: Diazirines are potentially explosive and should be handled with care.

3-Chloro-3-(trifluoromethyl)diazirine (1a). Diazirine **1a** was generated from trifluoroacetamide under Graham's conditions (hypochlorite and chloride ion in Me₂SO)¹⁶ as set forth by Moss et al.¹⁵ The sample was sublimed at -131 °C (10⁻⁶ Torr) and codeposited with argon to form a matrix: IR (Ar, 10 K) 1603 w, 1301 vs, 1213 vs, 1198 vs, 1082 w, 963 s, 739 m cm⁻¹.

3-Bromo-3-(trifluoromethyl)diazirine (1b). Diazirine **1b** was obtained from trifluoroacetamide under Graham's conditions (hypochlorite and bromide ion in Me₂SO)¹⁶ as performed by Dailey.¹⁷ The diazirine is rather stable in MCH solution at room temperature, decomposing slowly over a period of several days. The sample was sublimed at -131 °C (10⁻⁶ Torr) and codeposited with argon to form a matrix: IR (Ar, 10 K) 1598 m, 1291 s, 1208 vs, 1196 vs, 924 m, 725 m, 569 w cm⁻¹; UV/vis (MCH, 298 K) λ_{max} (rel OD) 336 (1.7), 321 (1.5), 307 (1.2), 295 (1.3), 234 (1.2), 274 sh (1.0), 208 (22.3) nm.

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(13) (a) Seburg, R. A.; McMahon, R. J. *J. Am. Chem. Soc.* 1992, 114, 7183-7189. (b) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* 1985, 107, 7597-7606.

(14) Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* 1943, 65, 1458-1460. (15) Moss, R. A.; Guo, W.; Denney, D. Z.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* 1981, 103, 6164-6169.

(16) Graham, W. H. *J. Am. Chem. Soc.* 1965, 87, 4396-4397.

(17) Dailey, W. P. *Tetrahedron Lett.* 1987, 28, 5801-5804.