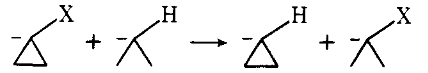
ular, the cyclopropyl anion shows a much more evenly balanced electron population distribution among the carbons in the bent configuration. The bent configurations in the $\alpha$-halocyclopropyl anions are characterized by a greater electron population on the halogen atom as compared to the planar anions. This additional electron population on the halogen is acquired at the expense of the hydrogens and the $\alpha$ carbon. In fact the $\alpha$ carbon ends up with a net decrease in electron population in the $\alpha$-fluorocyclopropyl anion. It is notable, however, that the other two carbons in the cyclopropyl ring retain their excess electron population on $\alpha$-halogen substitution. In fact there is an increasing discrepancy between the electron population on the $\alpha$ carbon and that on the other two carbons as X goes from hydrogen to chlorine and finally to fluorine.

In attempting to determine the relative stability of the three cyclopropyl anions we make use of the concept of the "isodesmic" reaction[13] of the type shown in eq 1. The energy of re-



(1)

action 1 represents the difference between halogen substituent stabilization of a strained ring and that of its saturated acyclic analogue. By calculating the total energies of all four species, using the same basis set (4-31G) and the same geometries for both rings and for both propanes, we obtain a reaction energy which should indicate whether the halogen has a stabilizing effect on the cyclopropyl anion or not. From the total energies listed in Table V we obtain a reaction energy of −1.8 kcal/mol when X is chlorine and −4.6 kcal/mol when X is fluorine. This suggests that substitution of hydrogen by chlorine may slightly destabilize the cyclopropyl anion whereas substitution by fluorine significantly destabilizes the anion. This pattern of increasing destabilization of the cyclopropyl anion follows the increasing discrepancy between the electron population on the $\alpha$ carbon and that on the other two carbons. However, the energy difference, particularly in the case of chlorine substitution, is so small that perhaps the only reasonable conclusion would be that the halogen substitution at the $\alpha$ carbon has little influence on the stability of the cyclopropyl anion.

In conclusion, therefore, our results show that the three cyclopropyl anions investigated all have substantial barriers to inversion of the X atom in $C_3H_4X^-$ about the plane of the cyclopropyl ring. This would certainly appear to support the idea of configuration retention in such ions. The effect of halogen substitution at the $\alpha$ carbon, while reducing the electron population in the ring, does so primarily at the expense of the $\alpha$ carbon leading to an imbalance of electron population distribution in the ring. The "isodesmic" reaction method suggests that such halogen substitution has only a small effect on the stability of the cyclopropyl anion and that the effect is a destabilizing one.

## Reference and Notes

(1) (a) C. Y. Meyers and V. M. Kolb, *J. Org. Chem.*, **43**, 1985 (1978); (b) C. Y. Meyers, W. S. Matthews, L. L. Ho, V. M. Kolb, and T. E. Parady in "Catalysis in Organic Syntheses", G. V. Smith, Ed., Academic Press, New York, 1977, pp 197–278; (c) C. Y. Meyers and V. M. Kolb, International Symposium on Chemistry of Strained Rings, SUNY-Binghamton, Binghamton, N.Y., May 27–29, 1977, Abstracts, p 28; (d) C. Y. Meyers, V. M. Kolb, and C. T. Webb, American Chemical Society Central Regional Meeting, Akron, Ohio, May 19–21, 1976, Abstracts, Phys. Org.-143; (e) V. M. Kolb, Ph.D. Dissertation, Southern Illinois University, Carbondale, Ill., 1976; (f) V. M. Kolb and C. Y. Meyers, 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1975, Abstract ORGN-88; (g) V. M. Kolb and C. Y. Meyers, American Chemical Society Midwest Regional Meeting, Carbondale, Ill., Oct. 1975, Abstract ORGN-505; (h) J. D. Dill, International Symposium on Chemistry of Strained Rings, SUNY-Binghamton, Binghamton, N.Y., May 27–29, 1977, Abstracts, p 27, reported a strain energy (kcal/mol) of 18.5 for cyclopropyllithium compared to 26.5 for cyclopropane.

(2) M. Charton in "The Chemistry of Alkenes", J. Zabicky, Ed., Wiley-Interscience, New York, 1970, Chapter 10.

(3) H. M. Walborsky, L. E. Allen, H. J. Traenckner, and E. J. Powers, *J. Org. Chem.*, **36**, 2937 (1971).

(4) G. W. Koeppl, D. S. Sagatys, G. S. Krishanamurthy, and S. I. Miller, *J. Am. Chem. Soc.*, **89**, 3396 (1967).

(5) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **14**, 370 (1969).

(6) M. J. S. Dewar, H. Metiu, P. J. Student, A. Brown, R. C. Bingham, D. H. Lo, C. A. Ramsden, H. Kollmar, P. Weiner, and P. K. Bischof, MINDO/3: General IBM Version, modified by M. L. Olson and J. F. Chiang, QCPE No. 309, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(7) W. J. Hehre, W. A. Lathon, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSSIAN 70, QCPE No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(8) H. H. Gunthard, R. C. Lord, and T. K. McCubbin, *J. Chem. Phys.*, **25**, 768 (1956).

(9) J. P. Friend and B. P. Dailey, *J. Chem. Phys.*, **29**, 557 (1958).

(10) C. C. Costain and G. B. B. M. Sutherland, *J. Phys. Chem.*, **56**, 321 (1952).

(11) R. E. Weston Jr., *J. Am. Chem. Soc.*, **76**, 2645 (1954).

(12) H. H. Jaffé, private communication.

(13) M. D. Newton in "Applications of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum Press, New York, 1977.

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# Infrared Spectra, Structure, and Bonding in the Dihalocarbene Cations in Solid Argon

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**Abstract:** Argon resonance photoionization of $CHFCl_2$, $CDFCl_2$, $CH_2Cl_2$, $CD_2Cl_2$, and $CHCl_3$ during condensation with excess argon at 15 K produced a new 1197-$cm^{-1}$ infrared absorption which is assigned to $CCl_2^+$. Chlorine and carbon-13 isotopic data verify the molecular identity and provide a 133° valence angle calculation. The markedly increased $\nu_3$ mode for $CCl_2^+$ at 1197 $cm^{-1}$ above $CCl_2$ at 746 $cm^{-1}$ is attributed to enhanced $\pi$ bonding in the cation. Observation of the $CClBr^+$ and $CBr_2^+$ cations at 1122 and 1019 $cm^{-1}$, respectively, in studies with $CH_2ClBr$ and $CHFBr_2$, $CDFBr_2$, $CH_2Br_2$, and $CD_2Br_2$ reinforces the identification of $CCl_2^+$.

Dihalocarbenes have been of considerable interest to physical organic chemists over the last 2 decades.[1] Dichlorocarbene has been trapped in solid argon following generation by photolysis, chemical reaction, and pyrolysis of suitable precursors.[2-4] Isotopic shifts in the matrix infrared spectrum provide a Cl-C-Cl bond angle determination[5] of 106 ± 5°, and the position of the infrared fundamentals of $CCl_2$ question the extent of $\pi$ bonding in this intermediate.[3] $\pi$ bonding should,

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however, be enhanced in the dichlorocarbene cation, and the vibrational spectrum of $CCl_2^+$ will help characterize the bonding in this species.

The dihalocarbene cation has been observed in numerous mass spectroscopic studies; $CCl_2^+$ is second to $CCl_3^+$ as the most abundant ion in the mass spectrum of $CCl_4$.[6] However, no other spectroscopic data is available for $CCl_2^+$.

Photoionization of halomethane reagents with argon discharge radiation during condensation at 15 K has trapped a number of parent and daughter ions for infrared and optical spectroscopic examination. Studies of $CCl_4$, $CF_3Cl$, and $CF_3Br$, for example,[7,8] gave spectra of daughter $CCl_3^+$, $CF_3^+$, $CF_2Cl^+$, and $CF_2Br^+$ and parent $CCl_4^+$, $CF_3Cl^+$, and $CF_3Br^+$ ions in solid argon, although no evidence for second daughter or "granddaughter" ions of the form $CX_2^+$ was obtained in these experiments. We report here infrared spectra in the 1000-1200-cm$^{-1}$ region from similar photoionization studies on $CHFX_2$ and $CH_2X_2$ matrix systems which provide the infrared spectrum of $CCl_2^+$ and its bromine-substituted counterparts.

## Experimental Section

The cryogenic refrigeration and vacuum system and matrix photoionization methods have been described previously.[7,9] The $CHFCl_2$ (Du Pont) and $CHFBr_2$ (Peninsular Chemresearch) precursors were vacuum distilled from glass beads to remove volatile impurities. The deuterium compound $CDFCl_2$ was synthesized by reacting $CDCl_3$ (Merck Sharp and Dohme) with $HgF_2$ for 30 min at 90 °C in a stainless steel tube; difluoro products were separated by vacuum distillation over glass beads. Carbon-13 enriched $CHFCl_2$ was synthesized from the reaction of $^{13}CHCl_3$ (90% $^{13}C$, Merck Sharp and Dohme) with $SbF_3/SbCl_5$ at 0 °C for 90 min followed by separation of the product on a preparative gas chromatograph.[10] Dibromofluoromethane-*d* was synthesized by reacting $CDBr_3$ with a $SbF_3/SbF_5$ (4/1) mixture at 25 °C for 60 min. The $CH_2X_2$ and $CHX_3$ precursors have been described in earlier reports.[11,12]

Samples of argon/precursor (400/1) were deposited on a CsI substrate at 15 K for 18-20 h with simultaneous irradiation from a windowless argon resonance lamp powered by a microwave discharge. Since a comparable amount of argon from the discharge was condensed with the sample, the $Ar/CHFX_2$ ratio in the matrix was double the sample value. The present experiments employed 1- and 3-mm orifice discharge tubes. Samples of each reagent were also deposited for 18-20 h without photoionization to measure precursor absorptions. Infrared spectra were recorded during and after sample deposition on expanded wavenumber scales using a Beckman IR-12. Samples were photolyzed with filtered BH-6-1 (Illumination Industries) high-pressure mercury arc light for 30-min periods, and additional expanded-scale spectra were scanned. Band intensities were measured in absorbance units and wavenumber accuracy is ±0.2 cm$^{-1}$ within a single scan.

## Results

Observations from matrix photoionization experiments on $CHFX_2$, $CH_2X_2$, and $CHX_3$ (X = Cl, Br) precursors will be described.

**Dihalofluoromethanes.** Two experiments were done with $Ar/CHFCl_2$ (400/1) samples using first 1-mm and then 3-mm orifice discharge tubes. The complete spectrum, similar to that reported by Jacox and Milligan,[13] has been analyzed in detail in a full study of the $CHFX_2$ isotopic compounds.[14] In the 1-mm tube experiment, a triplet was found at 1197, 1194, 1191 cm$^{-1}$ (*A* = absorbance units = 0.08, 0.05, 0.01) along with a strong 1179-cm$^{-1}$ absorption (*A* = 0.60); the former triplet increased and sharpened (*A* = 0.26, 0.17, 0.03) while the 1179-cm$^{-1}$ band was destroyed by 30 min of 220-1000-nm photolysis. The 1179-cm$^{-1}$ absorption, first assigned to $CHFCl^-$ by Jacox and Milligan,[13] has been reassigned[14] to the intramolecular hydrogen bonded anion Cl-H—(CFCl)$^-$, and the weak 1197-cm$^{-1}$ feature, unidentified in the previous work, is the subject of the present investigation. The 3-mm tube experiment produced a stronger triplet at 1197.1, 1194.3, 1191.5 cm$^{-1}$ (*A* = 0.27, 0.19, 0.04) and 1179 cm$^{-1}$ absorption (*A* ≈ 2.0). Photolysis with 290-1000-nm radiation increased the triplet by 10% and markedly reduced the 1179-cm$^{-1}$ absorption; this spectrum showing the prominent triplet, the remaining 1179-cm$^{-1}$ band labeled B, and absorption[15-17] due to CHFCl at 1251 cm$^{-1}$, CFCl at 1146 cm$^{-1}$, and $CFCl_2$ at 1144 cm$^{-1}$ are shown in Figure 1a. An experiment with an $Ar/^{13}CHFCl_2$ (600/1) sample and the 3-mm tube produced a sharp doublet at 1197.1, 1194.3 cm$^{-1}$, a weak 1179-cm$^{-1}$ feature (*A* = 0.16), and a strong 1151-cm$^{-1}$ counterpart (*A* ≈ 1.5). After photolysis, the 1151-cm$^{-1}$ $^{13}B$ absorption was reduced substantially, revealing a sharp doublet at 1158.1, 1155.3 cm$^{-1}$ (*A* = 0.13, 0.09), residual $^{13}B$ absorption at 1151 cm$^{-1}$ (*A* = 0.05), and the sharp doublet at 1197.1, 1194.3 cm$^{-1}$ (*A* = 0.02, 0.01) which are illustrated in Figure 1c. The analogous experiment with $CDFCl_2$ and a 3-mm discharge tube produced a sharp 1197, 1194 cm$^{-1}$ doublet on the side of a very strong 1180-cm$^{-1}$ species B absorption; the former was not affected by photolysis which markedly reduced the latter giving the infrared spectrum shown in Figure 1b.

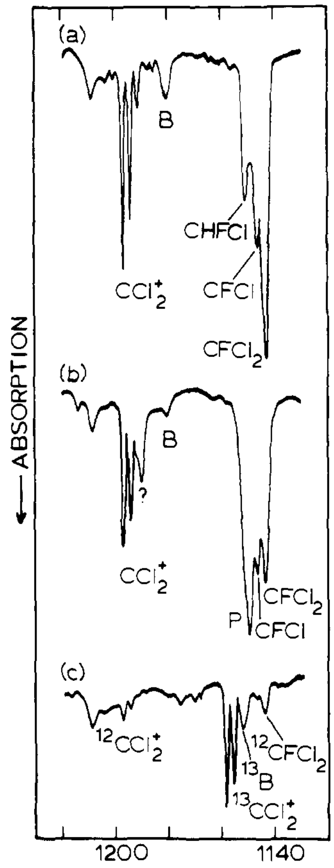

Figure 1. Infrared spectra in the 1140-1200-cm$^{-1}$ region of dichlorofluoromethane samples subjected to argon resonance photoionization from a 3-mm i.d. orifice discharge tube during condensation with excess argon at 15 K: (a) $Ar/CHFCl_2$ (400/1); (b) $Ar/CDFCl_2$ (400/1); (c) $Ar/^{13}CHFCl_2$ (600/1), 90% carbon-13. Illustrated spectra recorded after 420-1000, 340-600, and 220-1000 nm high-pressure mercury arc photolysis sequence.

Two experiments with $CHFBr_2$ using the 3-mm tube produced a strong, sharp 1019.5-cm$^{-1}$ absorption (*A* = 0.36) which was decreased to *A* = 0.16 by 290-1000-nm photolysis. Two similar experiments with $CDFBr_2$ gave the same sharp 1019.5-cm$^{-1}$ band (*A* = 0.28) which exhibited identical photolysis behavior. Similar experiments with the 1-mm tube produced weaker 1019.5-cm$^{-1}$ bands (*A* = 0.07).

**Dihalomethanes.** Previous experiments with $CH_2Cl_2$ in this laboratory using a 1-mm orifice discharge tube produced a

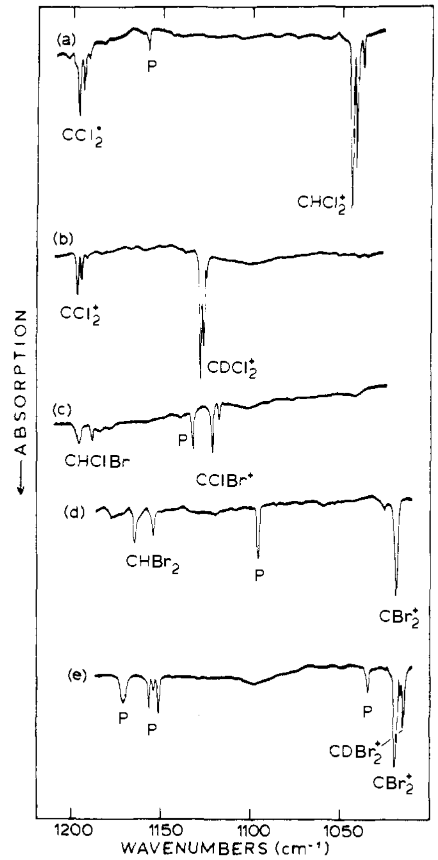

**Figure 2.** Infrared spectra in the 1020–1200-$cm^{-1}$ region of methylene halide samples $Ar/CH_2X_2$ (400/1) subjected to argon resonance photoionization from 1-2-mm i.d. orifice discharge tubes during condensation with excess argon at 15 K: (a) $CH_2Cl_2$; (b) $CD_2Cl_2$; (c) $CH_2ClBr$, illustrated spectra recorded after 420–1000, 340–600, 290–1000, 220–1000 nm photolysis sequence; (d) $CH_2Br_2$; (e) $CD_2Br_2$, illustrated spectra recorded after 650–1000-nm photolysis for 30 min.

weak 1194-$cm^{-1}$ band which photolyzed with red light revealing a new 1197, 1194 $cm^{-1}$ product absorption not discussed in the earlier report,[11] which is of particular interest in this study for comparison to the 1197-$cm^{-1}$ product band in the above $CHFCl_2$ studies. An experiment with a 2-mm orifice tube gave a lower yield of the photosensitive 1194- and 764-$cm^{-1}$ bands, assigned to $CH_2Cl_2^+$ in the earlier report, and a higher yield of the 1197-$cm^{-1}$ absorption. After 290–1000-nm photolysis, three isotopic components were resolved at 1196.8, 1194.0, 1191.4 $cm^{-1}$ ($A$ = 0.10, 0.06, 0.01), and the 1045.4, 1042.5, 1039.8 $cm^{-1}$ triplet, assigned to the $CHCl_2^+$ daughter cation, was increased.[11] The 1000–1200-$cm^{-1}$ region from the previous infrared investigation is shown in Figure 2a to provide more information on the new 1197-$cm^{-1}$ absorption. An experiment was done with $CH_2Cl_2$ using the 3-mm orifice discharge tube. The yield of the 1196.8, 1194.0, 1191.4 $cm^{-1}$ triplet was slightly reduced ($A$ = 0.06, 0.05, 0.01) and the $CH_2Cl_2^+$ band at 764 $cm^{-1}$ was very weak ($A$ = 0.01). Full arc photolysis for 35 min increased the 1197-$cm^{-1}$ absorption slightly ($A$ = 0.07, 0.04, 0.01). A $CD_2Cl_2$ experiment using a 2-mm orifice discharge tube produced an identical 1196.8, 1194.0, 1191.4 $cm^{-1}$ triplet, but the $CDCl_2^+$ absorption shifted to 1128.0, 1226.3, 1224.8 $cm^{-1}$, which is illustrated in Figure 2b. The $^{13}CH_2Cl_2$ experiments[11] produced weak, sharp new product bands at 1158 and 1155 $cm^{-1}$, which increased on 220–1000-nm photolysis revealing a weaker 1152-$cm^{-1}$ partner; the 1158-$cm^{-1}$ product appeared on top of a very weak 1158-$cm^{-1}$ $^{13}CH_2Cl_2$ precursor absorption.

An investigation with $CH_2ClBr$ produced sharp, weak 1166-, 1122-, and 993-$cm^{-1}$ absorptions. Red photolysis destroyed the 1166-$cm^{-1}$ feature, Pyrex-filtered photolysis produced a sharp 993.5, 989.0 $cm^{-1}$ doublet ($A$ = 0.14, 0.045) assigned to $CHClBr^+$,[11] and full arc photolysis halved the $CHClBr^+$ features, increased CHClBr radical absorptions[18] at 1196, 1188, 866, and 861 $cm^{-1}$, and produced a sharp, new unidentified doublet at 1122.0, 1118.0 $cm^{-1}$ ($A$ = 0.06, 0.02).[11] The latter spectrum is shown in Figure 2c.

The details of several methylene bromide experiments have been reported previously.[11] A sharp, unidentified 1019.5-$cm^{-1}$ ($A$ = 0.30) product band is of particular interest here. Red photolysis (650–1000 nm) destroyed the weak 1129-$cm^{-1}$ absorption assigned to $CH_2Br_2^+$ and left the rest of the bands unchanged; this spectrum[11] containing 1155, 1165 $cm^{-1}$ $CHBr_2$ radical absorptions[18] is illustrated in Figure 2d to contrast the bromine-substituted counterparts of the 1197-$cm^{-1}$ chlorine species. Full arc photolysis reduced the 1019.5-$cm^{-1}$ band ($A$ = 0.16). A sharp, unshifted 1019.5-$cm^{-1}$ product band with similar behavior was observed in the $CD_2Br_2$ experiment,[11] which, along with $CDBr_2^+$ at 1015 $cm^{-1}$, is shown in Figure 2e.

**Trihalomethanes.** A thorough study of the chloroform-bromoform series of compounds has been performed in this laboratory.[12] The most productive $CHCl_3$ experiment also produced a weak 1197-$cm^{-1}$ absorption ($A$ = 0.01). Studies with $CHCl_2Br$ and $CHClBr_2$ revealed weak 1122-$cm^{-1}$ bands ($A$ = 0.01 and 0.02). The most productive $CHBr_3$ study also gave a weak 1019.5-$cm^{-1}$ product band ($A$ = 0.02).

## Discussion

The new product absorptions will be identified and the structure, bonding, and mechanism of formation for this new molecular cation will be discussed.

**Identification of $CCl_2^+$.** The sharp, new resolved triplet measured at 1197.1, 1194.3, 1191.5 $cm^{-1}$ in matrix photoionization studies of $CHFCl_2$ is in excellent agreement with the 1196.8, 1194.0, 1191.4 $cm^{-1}$ triplet observed in similar studies with $CH_2Cl_2$ which suggests that a common fragment is responsible for this new absorption. A weak 1197-$cm^{-1}$ feature was also found in $CHCl_3$ work. The relative intensities in the triplet correspond to the 9/6/1 ratio expected for a vibration of two equivalent chlorine atoms with natural-abundance $^{35}Cl$ and $^{37}Cl$ isotopes. The 90% carbon-13 enriched $^{13}CHFCl_2$ study produced the $^{12}C^{35}Cl_2$, $^{12}C^{35}Cl^{37}Cl$, $^{13}C^{35}Cl_2$, and $^{13}C^{35}Cl^{37}Cl$ isotopes with intensities indicative of a single carbon species. The deuterated precursors gave the exact same (±0.2 $cm^{-1}$) triplet, which shows that the new product species does not contain deuterium; this evidence is particularly significant for a mode in the hydrogen deformation region since deuterium substitution changes the mixing of C–H deformation and carbon–halogen stretching modes and produces a large shift *if* H is present in the species. A graphic example is provided by the $CHCl_2^+$ and $CDCl_2^+$ species shown in Figure 2a,b which exhibit a large 83-$cm^{-1}$ displacement on deuterium substitution.[11] Thus, the isotopic data identify a new ($CCl_2$) molecular species.

The new product in $CH_2ClBr$ experiments exhibited a 3/1 doublet absorption at 1122, 1118 $cm^{-1}$ which is precisely that expected for the vibration of a single chlorine atom species with chlorine isotopes in natural abundance. The sharp single 1019.5-$cm^{-1}$ feature in the $CHFBr_2$, $CH_2Br_2$, $CDFBr_2$, $CD_2Br_2$, and $CHBr_3$ experiments, of course, does not involve chlorine nor does it involve hydrogen; bromine isotopic splittings are too small to be resolved. The observation of three product absorptions, 1197, 1122, 1019 $cm^{-1}$, from the three precursors $CH_2Cl_2$, $CH_2ClBr$, and $CH_2Br_2$ confirms that the new product species contains two equivalent halogen atoms, in agreement with the chlorine isotopic splittings.

The neutral dichlorocarbene $\nu_3$ absorption has been well documented at 746 $cm^{-1}$ in solid argon.[2-4] The significantly higher 1197-cm$^{-1}$ absorption is also above antisymmetric C-Cl$_2$ stretching modes for CHCl$_2^+$ at 1045 cm$^{-1}$ and CFCl$_2^+$ at 1142 cm$^{-1}$,[11,19] which point to assignment of the 1197-cm$^{-1}$ triplet to $\nu_3$ of CCl$_2^+$ in solid argon. The 1122, 1118 cm$^{-1}$ doublet is assigned to CClBr$^+$ and the 1019-cm$^{-1}$ absorption to CBr$_2^+$, in this series of dihalocarbene cations, which are above the analogous CHClBr$^+$ and CHBr$_2^+$ absorptions at 993 and 897 cm$^{-1}$, respectively.[11]

A photosensitive 927-cm$^{-1}$ absorption in proton radiolysis studies of CCl$_4$ was first assigned to CCl$_2^+$ and then reassigned to an asymmetric CCl$_2$Cl$_2^+$ parent ion owing to its photochemical behavior.[6,7] Appearance potentials[20] show that the process CCl$_2^+$ → CCl$^+$ + Cl requires 6.5 eV, which is above the mercury arc energy. Hence CCl$_2^+$ cannot photodissociate in these experiments. Although photodetachment of electrons from chloride ion traps and partial neutralization of CCl$_2^+$ may be expected on prolonged 220-1000-nm photolysis of these samples,[21] photobleaching of CCl$_2^+$ will probably not reduce CCl$_2^+$ absorptions until CHCl$_2^+$, a possible photochemical precursor of CCl$_2^+$, is also destroyed. The stability of the 1197-cm$^{-1}$ triplet on mercury arc photolysis is consistent with its assignment to CCl$_2^+$.

**Structure.** The chlorine isotopic triplet indicates two equivalent chlorine atoms. For a symmetrical triatomic, sets of isotopic $\nu_3$ fundamentals provide a basis for calculation of the bond angle. The 1197.1- and 1158.1-cm$^{-1}$ assignments for $^{12}$C$^{35}$Cl$_2^+$ and $^{13}$C$^{35}$Cl$_2^+$ give a Cl-C-Cl angle of 136° and the $^{12}$C$^{35}$Cl$_2^+$ and $^{12}$C$^{37}$Cl$_2^+$ observations at 1197.1 and 1191.5 cm$^{-1}$ provide a 130° value. The average value 133°, with estimated ±8° error limits, should be reliable for CCl$_2^+$. Similar calculations for CCl$_2$ neutral give a 106° average angle. Removal of one electron is expected to increase the bond angle; this relationship is illustrated by the 18- and 17-electron molecules O$_3$ (117°) and NO$_2$ (134°), respectively.

**Bonding.** The substantial increase in $\nu_3$ fundamental from 746 cm$^{-1}$ for CCl$_2$ on ionization to 1197 cm$^{-1}$ for CCl$_2^+$ is perhaps more than expected, although considerable increases have been observed for CHCl$_2$ to CHCl$_2^+$ (902 to 1045 cm$^{-1}$)[11] and CFCl$_2$ to CFCl$_2^+$ (919 to 1142 cm$^{-1}$).[19] Part of the increase in $\nu_3$ for CCl$_2^+$ is probably due to increased stretch-stretch interaction owing to the larger valence angle. Although a complete C-Cl bond force constant analysis for CCl$_2^+$ requires both $\nu_1$ and $\nu_3$ fundamentals, it is clear that the C-Cl stretching force constant for CCl$_2^+$ will be substantially higher than for CCl$_2$. The electron removed from CCl$_2$ on ionization is probably a chlorine lone pair electron; this vacancy may facilitate contraction of the chlorine 3p orbital and make Cl 3p-C 2p overlap more favorable for $\pi$ bonding in CCl$_2^+$. The increased Cl-C-Cl valence angle also increases the capability for $\pi$ bonding in the cation. Both of the above points help explain the substantial increase in the $\nu_3$ fundamental for CCl$_2^+$ as compared to CCl$_2$.

It is also of interest to contrast the analogous difluorocarbene cation, which has been produced in CHF$_3$ photoionization experiments in this laboratory and now can be identified after considering the above case for CCl$_2^+$. A sharp 1588-cm$^{-1}$ absorption with a 1585-cm$^{-1}$ site splitting shifted to 1550.5 cm$^{-1}$ upon carbon-13 substitution and exhibited no deuterium shift; this absorption is probably due to CF$_2^+$. The 1588-cm$^{-1}$ absorption is considerably higher than CF$_2$ at 1222 and 1101 cm$^{-1}$ but slightly below CHF$_2^+$ at 1608 cm$^{-1}$,[22,23] in contrast to CCl$_2^+$, which absorbs considerably higher than CHCl$_2^+$. Two differences between CF$_2$ and CCl$_2$ are worthy of note. First, ionization at 11.4 eV in the former comes from an (a$_1$) orbital which is primarily from the carbon lone pair[24] whereas ionization of the latter at 9.8 eV[25] almost surely involves a chlorine lone-pair electron, and accordingly the $\pi$ bonding in CF$_2^+$ and CCl$_2^+$ will be somewhat different. The proton affinity of CF$_2$, 172 ± 2 kcal/mol,[26] is lower than the proton affinity of CCl$_2$, 208 ± 2 kcal/mol,[27] which is consistent with CF$_2$ being more stable than CCl$_2$. It is suggested that CCl$_2^+$ gains more electronic stabilization on ionization than does CF$_2^+$ based on the relative positions of the CX$_2^+$ and CHX$_2^+$ antisymmetric C-X$_2$ stretching fundamentals.

A MINDO/3 calculation performed by Lowe for CCl$_2$ and CCl$_2^+$ showed that the optimum valence angle for the cation is 30° larger than for the neutral carbene. The C-Cl bond length is 0.09 Å *shorter* in the cation since the electron is removed from a molecular orbital that is strongly C-Cl antibonding.[28] The MINDO/3 calculation is consistent with the infrared data on CCl$_2^+$.

**Mechanism of Formation.** Dichlorocarbene has been observed as a photolysis product at 746 cm$^{-1}$ in the CD$_2$Cl$_2$ experiments, but this absorption was masked by a parent band in CH$_2$Cl$_2$ studies. The most probable method of formation of CCl$_2^+$ in these experiments is by direct argon resonance photoionization of the CCl$_2$ intermediate, reaction 1, which requires 9.8 eV in the gas phase.[25]

$$\mathrm{CCl_2} + h\nu\ (11.6\text{-}11.8\ \mathrm{eV}) \rightarrow \mathrm{CCl_2^+} + e^- \qquad (1)$$

Although CCl$_2$ was not observed in the infrared studies with CHFCl$_2$, its presence has been verified by optical absorption spectra,[13,14] and reaction 1 is also a likely route to CCl$_2^+$ in experiments with CHFCl$_2$.

The CCl$_2^+$ yield is, however, a factor of 3 greater in CHFCl$_2$ relative to CH$_2$Cl$_2$ experiments, which suggests an additional mechanism for the formation of CCl$_2^+$ with the CHFCl$_2$ precursor. Optical and infrared spectra suggest that the CHFCl$_2^+$ and CHFBr$_2^+$ parent ions are also formed in these experiments.[14] Another mechanism for the production of CCl$_2^+$ is by HF photoelimination from the parent cation, reaction 2. The dibromocarbene cation is produced by reactions analogous to (1) and (2). The larger yield of the 1019-cm$^{-1}$ band in these experiments is consistent with higher cross sections for the production of CBr$_2^+$.

$$\mathrm{CHFCl_2^+} + h\nu\ (11.6\text{-}11.8\ \mathrm{eV}) \rightarrow \mathrm{CCl_2^+} + \mathrm{HF} \qquad (2)$$

The substantial increase in the CClBr$^+$ doublet on 220-1000-nm photolysis suggests a photochemical route for the production of these dihalocarbene cations. The photolysis of the parent cations and the formation of the first daughter ions CHX$_2^+$ have been discussed in the previous report.[11] Full arc photolysis of these samples increases CClBr$^+$ at the expense of CHClBr$^+$, reaction 3. In addition CHClBr radical bands increased, which shows that photoneutralization of CHClBr$^+$ by electron detachment from bromide or chloride ions is a competing process.

$$\mathrm{CHClBr^+} + h\nu\ (220\text{-}1000\ \mathrm{nm}) \rightarrow \mathrm{CClBr^+} + \mathrm{H} \qquad (3)$$

## Conclusions

Dichlorocarbene cation has been observed at 1197 cm$^{-1}$ in matrix photoionization experiments with CHFCl$_2$, CH$_2$Cl$_2$, and CHCl$_3$. Resolved chlorine isotopic splittings and large carbon-13 and no deuterium isotopic shifts verify the molecular identity. The antisymmetric carbon-chlorine absorption for CCl$_2^+$ at 1197 cm$^{-1}$ is higher than this mode for CHCl$_2^+$ at 1045 cm$^{-1}$ and substantially higher than CCl$_2$ at 746 cm$^{-1}$. This increase is attributed to significantly enhanced $\pi$ bonding in the cation. Isotopic shifts show that the Cl-C-Cl valence angle is increased 25-30° on ionization. The analogous CClBr$^+$ and CBr$_2^+$ cations were observed at 1122 and 1019 cm$^{-1}$, respectively. This work is of interest as the first infrared observation of a second daughter cation.

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## References and Notes

(1) (a) W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press, New York, 1971; (b) M. Jones and R. A. Moss, "Carbenes", Vol. 1, Wiley, New York, 1973; (c) D. Bethell in "Organic Reactive Intermediates", S. P. McManus, Ed., Academic Press, New York, 1973, Chapter 2; (d) J. Hine, "Divalent Carbon", Ronald Press, New York, 1964.

(2) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **47**, 703 (1967).

(3) L. Andrews, *J. Chem. Phys.*, **48**, 979 (1968).

(4) A. K. Maltsev, R. H. Hauge, and J. L. Margrave, *J. Phys. Chem.*, **75**, 3984 (1971).

(5) D. A. Hatzenbuhler, L. Andrews, and F. A. Carey, *J. Am. Chem. Soc.*, **97**, 187 (1975).

(6) L. Andrews, J. M. Grzybowski, and R. O. Allen, *J. Phys. Chem.*, **79**, 904 (1975).

(7) F. T. Prochaska and L. Andrews, *J. Chem. Phys.*, **67**, 1091 (1977).

(8) F. T. Prochaska and L. Andrews, *J. Am. Chem. Soc.*, **100**, 2102 (1978).

(9) C. A. Wight, B. S. Ault, and L. Andrews, *J. Chem. Phys.*, **65**, 1244 (1976).

(10) L. Andrews, H. Willner, and F. T. Prochaska, *J. Fluorine Chem.*, **13**, 273 (1979).

(11) L. Andrews, F. T. Prochaska, and B. S. Ault, *J. Am. Chem. Soc.*, **101**, 9, (1979).

(12) L. Andrews, C. A. Wight, F. T. Prochaska, S. A. McDonald, and B. S. Ault, *J. Mol. Spectrosc.*, **73**, 120 (1978).

(13) M. E. Jacox and D. E. Milligan, *Chem. Phys.*, **16**, 195 (1976).

(14) B. W. Keelan and L. Andrews, to be published.

(15) F. T. Prochaska, B. W. Keelan, and L. Andrews, *J. Mol. Spectrosc.*, to be published.

(16) C. E. Smith, D. E. Milligan, and M. E. Jacox, *J. Chem. Phys.*, **54**, 2780 (1971).

(17) D. E. Milligan, M. E. Jacox, J. H. McAuley, and C. E. Smith, *J. Mol. Spectrosc.*, **45**, 377 (1973).

(18) T. G. Carver and L. Andrews, *J. Chem. Phys.*, **50**, 4235 (1969).

(19) F. T. Prochaska and L. Andrews, *J. Chem. Phys.*, **68**, 5568 (1978).

(20) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6**, No. 1 (1977).

(21) F. T. Prochaska and L. Andrews, *J. Chem. Phys.*, **68**, 5577 (1978).

(22) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **48**, 2265 (1968).

(23) L. Andrews and F. T. Prochaska, *J. Phys. Chem.*, **83**, 824 (1979).

(24) J. M. Dyke, L. Golob, N. Jonathan, A. Morris, and M. Okuda, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1828 (1974).

(25) J. S. Shapiro and F. P. Lossing, *J. Phys. Chem.*, **72**, 1552 (1968).

(26) J. Vogt and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 6682 (1975).

(27) B. A. Levi, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 8454 (1977).

(28) J. P. Lowe, unpublished calculation (1979).

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# Selective Naked-Cluster Cryophotochemistry and SCF-X$\alpha$-SW Calculations for $Cu_2$ and $Ag_2$

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**Abstract:** The concept of conducting photoselective transformations on small, well-defined, ligand-free transition metal clusters is explored for the first time by investigating the visible (370–390 nm) photochemistry of Ar- and Kr-entrapped $Cu_2$ and $Ag_2$. With prior knowledge of the 200–900-nm optical spectra of $Cu_{1-3}$ and $Ag_{1-4}$ clusters, generated either by metal atom deposition or photoclustering techniques, one can rationalize the observed $Cu_2$ and $Ag_2$ visible cryophotochemistry in terms of a highly selective matrix-induced photodissociation step for which a mechanism involving formation of a metal atom–matrix atom(s) exciplex is proposed. SCF-X$\alpha$-SW MO calculations for $Cu_2$ and $Ag_2$ confirm that the wavelengths used for the photoexcitations are essentially those of the electronic transitions from the main bonding to the main antibonding orbital (i.e., $s\sigma_g \rightarrow s\sigma_u$), thus providing a description of the excited states which is useful in accounting for the observed photochemistry. The calculations represent the most thorough theoretical study of $Cu_2$ and $Ag_2$ to date. Complete potential curves are calculated and the observed $r_e$, $D_e$, and $\nu$(M–M) are in good agreement with experiment. The bonding at the likely equilibrium distances is discussed; that in $Ag_2$ is found to be almost purely s, while in $Cu_2$ there appears to be a minor d contribution. The electronic spectra are assigned in detail from transition-state calculations of both energies and oscillator strengths. The $A \leftarrow X$, $C \leftarrow X$, and $E \leftarrow X$ systems of $Ag_2$ are attributed to $s\sigma \rightarrow s\sigma^*$, $s\sigma \rightarrow p\pi$, and $d\pi^* \rightarrow s\sigma^*$ transitions, respectively. The $A \leftarrow X$ and $B \leftarrow X$ systems of $Cu_2$ are ascribed to $d\pi^* \rightarrow s\sigma^*$ and $s\sigma \rightarrow s\sigma^*$ excitations, and the UV bands of $Cu_2$ near 260, 235, and 220 nm are assigned to mainly $d\pi^* \rightarrow p\pi$, $s\sigma \rightarrow p\pi$, and $d\sigma \rightarrow s\sigma^*$ processes, respectively.

## Introduction

Recent work in our laboratory has demonstrated that small metallic[1] and bimetallic[2] clusters of known composition can be efficiently generated in low-temperature, weakly interacting matrix supports by narrow-band photoexcitation of the resonance lines of matrix-entrapped metal atomic species. The highly controlled nature and photoselectivity of the aggregation processes involved have recently been unveiled in a series of M/M′/Ar(Kr) bimetallic experiments[2,3] (where M = Cr; M′ = Mo or Ag) in which the following sequence of nucleation events was observed:

$$\left.\begin{array}{l} M^{\dagger} + M^{\dagger} \rightarrow M_2 \\ M^{\dagger} + M_2 \rightarrow M_3 \\ M^{\dagger} + MM' \rightarrow M_2M' \\ M^{\dagger} + M' \rightarrow MM' \\ M^{\dagger} + M'_2 \rightarrow MM'_2 \end{array}\right\} \text{M photomobilization (no } M'_2,\ M'_3 \text{ clusters observed)}$$

$$\left.\begin{array}{l} M'^{\dagger} + M'^{\dagger} \rightarrow M'_2 \\ M'^{\dagger} + M'_2 \rightarrow M'_3 \\ M'^{\dagger} + MM' \rightarrow MM'_2 \\ M'^{\dagger} + M \rightarrow MM' \\ M'^{\dagger} + M_2 \rightarrow M_2M' \end{array}\right\} \text{M' photomobilization (no } M_2,\ M_3 \text{ clusters observed)}$$

(where $M^{\dagger}$ and $M'^{\dagger}$ represent photomobilized M and M′, respectively).

Recent emission experiments by Kolb and co-workers[4a] and Ozin, Kenney-Wallace, and co-workers,[4c] employing 300–330-nm excitation of Ag atoms in inert gas matrices, have revealed the presence of several intense emission bands. In the cases of argon and krypton the largest Stokes shift corresponds to the most intense band which is centered in the region 400–500 nm. The large Stokes shift suggests the existence of a significant nonradiative energy channel following Ag atom photoexcitation, of which the observed metal atom photomobility is presumably a manifestation. At the present time we

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