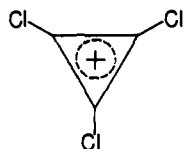


The Trichlorocyclopropenium Ion¹

Sir:

The reaction of tetrachlorocyclopropene² with strong Lewis acids may lead either to the formation of stable salts of the trichlorocyclopropenium ion (1) or to cyclopropene products which can most reasonably be explained by assuming the intermediate formation of this ion.



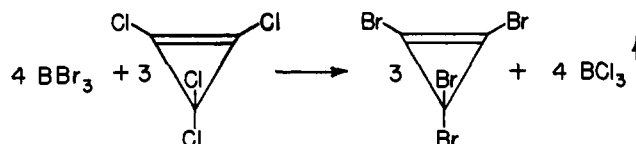
Gentle warming of a mixture of AlCl_3 and excess tetrachlorocyclopropene initiates an exothermic reaction which results in the formation of a new white powder (2). The analysis of this solid after removal of excess tetrachlorocyclopropene under vacuum agrees with that of trichlorocyclopropenium tetrachloroaluminate, $\text{C}_3\text{Cl}_3^+\text{AlCl}_4^-$. *Anal.* Calcd.: C, 11.59; Cl, 79.72; Al, 8.69; H, 0.00. Found: C, 11.48; Cl, 79.61; Al, 8.80; H, 0.09. The infrared spectrum of the solid (Nujol mull) between 4000 and 350 cm^{-1} shows just four bands at 1350 (m,s), 1315 (vs,b), 731 (m,s), and 482 (vs,b) cm^{-1} , indicating a highly symmetrical system. The intense bands for the parent tetrachlorocyclopropene at 1155, 1053, and 617 cm^{-1} are absent. Similarly, treatment of liquid SbCl_5 with excess tetrachlorocyclopropene yields on work-up a white solid (3) which has an analysis corresponding to trichlorocyclopropenium hexachloroantimonate, $\text{C}_3\text{Cl}_3^+\text{SbCl}_6^-$. *Anal.* Calcd.: C, 7.55; Cl, 66.95; Sb, 25.50. Found: C, 7.40; Cl, 66.0; Sb, 26.6 (by difference). This material has an infrared spectrum in the region 4000–350 cm^{-1} (Nujol mull) with just three bands at 1348 (s,s), 1313 (vs,b), and 735 (m,s) cm^{-1} . This spectrum is essentially identical with that of 2, except the band at 482 cm^{-1} is absent.

Compound 2 dissolves readily in liquid SO_2 without decomposition and on cooling to -78° redeposits in large well formed colorless crystals, m.p. $157\text{--}159^\circ$ dec. That the integrity of the three-membered ring is preserved in these reactions is shown by the fact that quenching either 2 or 3 in water regenerates tetrachlorocyclopropene in 60+% yield.

If molecular adducts or π -complexes were produced in the reactions of tetrachlorocyclopropene with AlCl_3 and SbCl_5 , it is most unlikely that the spectra of the two products would be so strongly similar or so simple. On the other hand, the data are entirely consistent with the formation of ionic products involving the trichlorocyclopropenium ion. Of the four bands observed for 2, the one at 482 cm^{-1} may then be assigned to AlCl_4^- . Solid sodium tetrachloroaluminate,³ which is known to

be ionic and contain tetrahedral AlCl_4^- anions,⁴ shows just one infrared band in the region 4000–350 cm^{-1} (Nujol mull) at 481 (vs,b) cm^{-1} .⁵ The remaining three bands common to 2 and 3 are in reasonable positions for the trigonal planar (D_{3h}) trichlorocyclopropenium ion, which is predicted to have four infrared active fundamentals of which one would be expected to occur below 300 cm^{-1} .

When BBr_3 is added to tetrachlorocyclopropene, no stable salt precipitates. Instead, a vigorous reaction occurs which liberates BCl_3 . The reaction proceeds as rapidly as the reagent is added up to the point where almost all the tetrachlorocyclopropene has been converted to tetrabromocyclopropene (4) according to the equation



Small amounts of mixed bromochlorocyclopropenes can be detected in the product mixture at the end of the reaction using vapor phase chromatography. These results can best be explained by assuming a reaction mechanism which involves the intermediate formation of mixed bromochlorocyclopropenium ions.

Tetrabromocyclopropene is a colorless liquid (n_D^{25} 1.6344) which is best purified by preparative gas chromatography. *Anal.* Calcd.: C, 10.21; Br, 89.99. Found: C, 10.53; Br, 89.01. The infrared spectrum of 4 in the NaCl region (liquid film) shows bands at 1757 (m,s) (cyclopropene $\text{C}=\text{C}$), 1135 (s,s), 1121 (vs,s), 1075 (m,s), 1002 (vs,b), and 664 (vs,b) cm^{-1} .

Treatment of tetrabromocyclopropene with Br_2 under ultraviolet irradiation converts it rapidly and quantitatively to hexabromocyclopropane (5), m.p. $194\text{--}196^\circ$. *Anal.* Calcd.: C, 6.80; Br, 93.20; H, 0.00. Found: C, 7.08; Br, 93.05; H, 0.00. The infrared spectrum of 5 in the NaCl region (Nujol mull) shows bands at 862 (s,s), 719 (vs,s), 677 (s,s), and 651 (m,s) cm^{-1} .

The trichlorocyclopropenium ion is an example of the simplest possible carbocyclic aromatic system (six atoms, two kinds) and complete analysis of the infrared and Raman spectra of this ion should provide additional insight into the bonding in cyclopropenium systems.⁶ Further work on other chemical reactions of this ion is in progress and will be the subject of further communications.

(4) N. C. Baenziger, *Acta Cryst.*, **4**, 216 (1951).

(5) G. L. Carlson, *Spectrochim. Acta*, 1291 (1963), lists the band for AlCl_4^- in solid $\text{PCl}_4^+\text{AlCl}_4^-$ at 490 cm^{-1} and summarizes the results on molten $\text{Na}^+\text{AlCl}_4^-$ obtained by Gerding and Houtgraaf.³

(6) See M. Sundaralingam and L. H. Jensen, *J. Am. Chem. Soc.*, **85**, 3302 (1963).

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(1) Presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

(2) S. Tobey and R. West, *Tetrahedron Letters*, 1179 (1963).

(3) H. Gerding and H. Houtgraaf, *Rec. Trav. chim.*, **72**, 21 (1953).

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